State of Safety Study in Tsinghua University

Xuning Feng, Dongsheng Ren,
Minggao Ouyang*, Languang Lu, Xiangming He

PCG, Department of Automotive of Engineering
Tsinghua University

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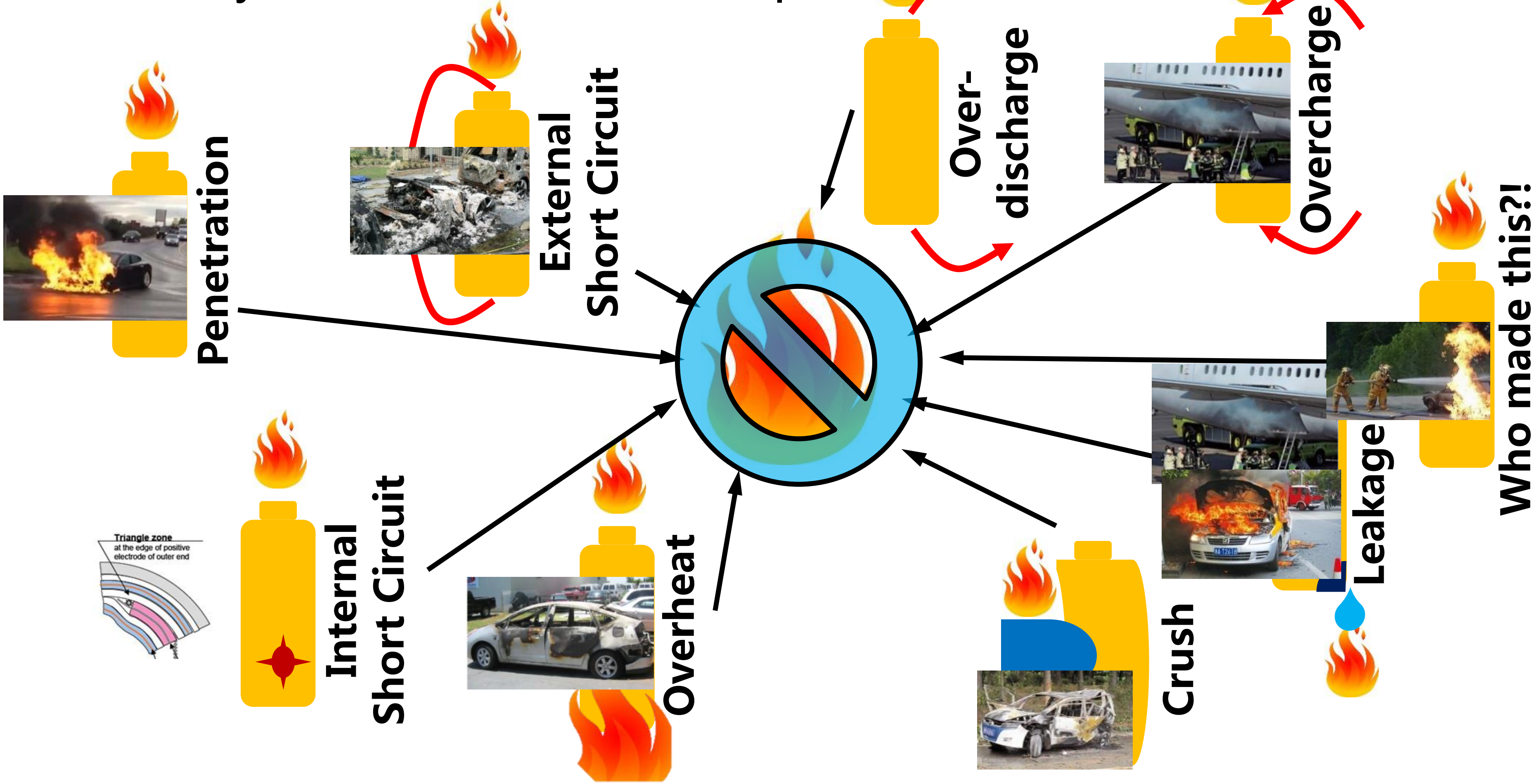
Backgrounds

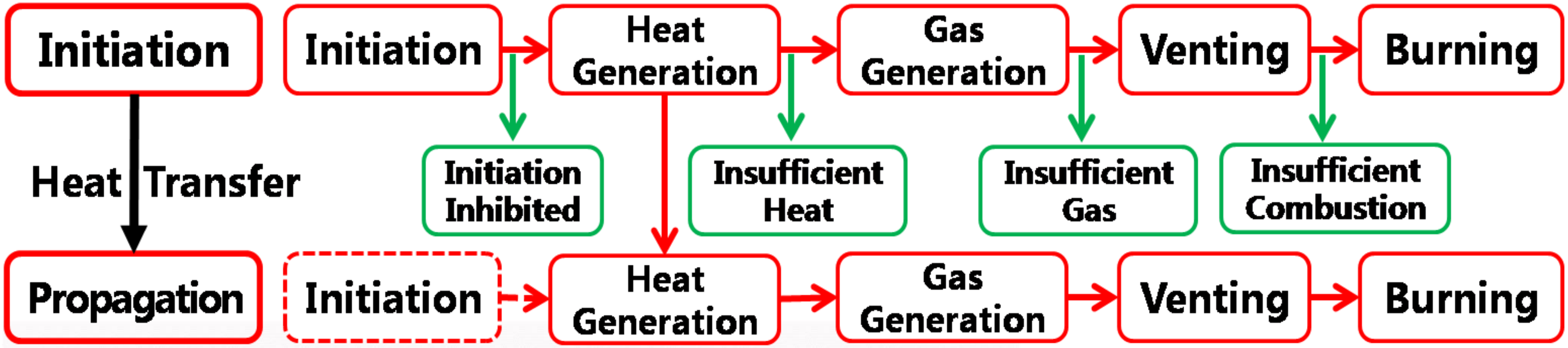
Practically, not fire free with QC pass.

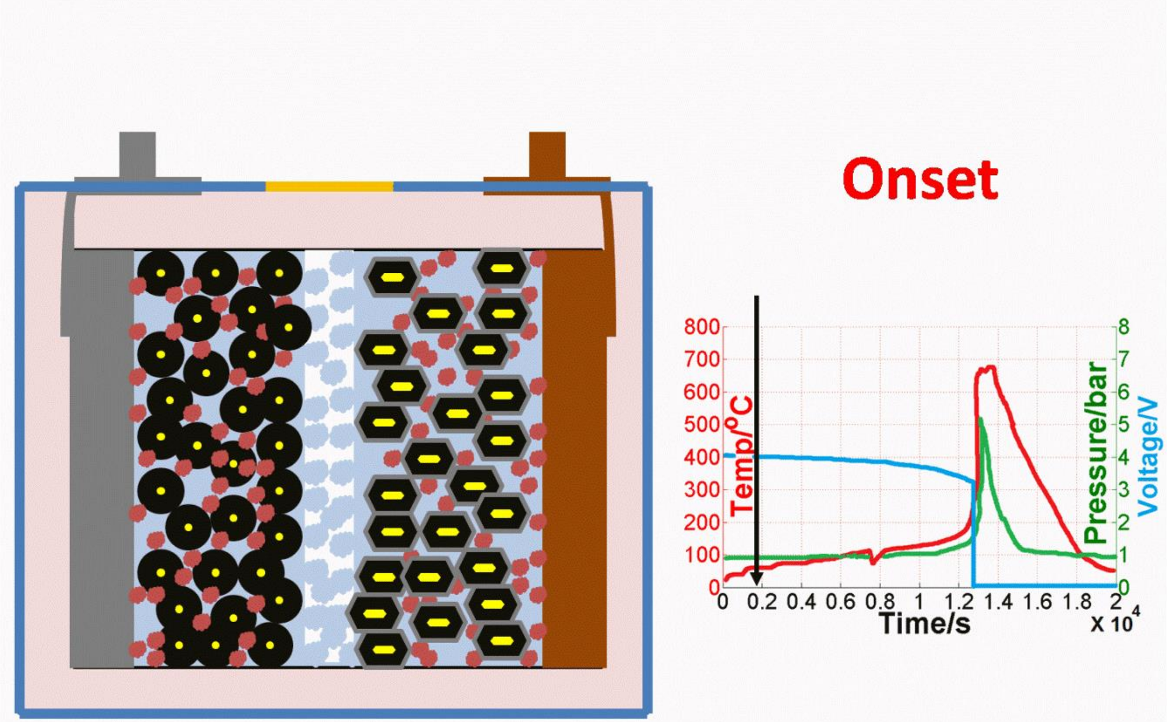


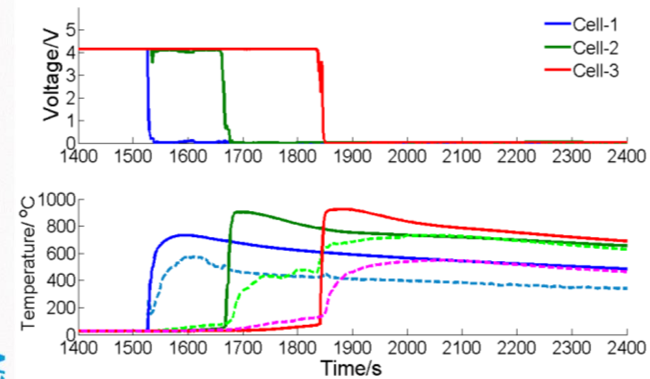
All included in compulsory test profiles for Li-ion battery in different areas:

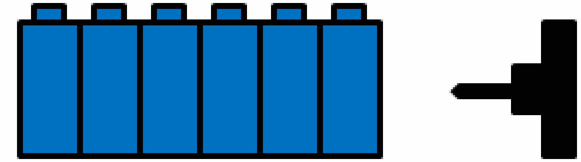
➢ *QCT 743, IEC 62660, IEC 62133, UL 1642, UL 2054, UL 2580, SAE J2464, SAE J1929, ISO/WD 12405, JIS 8711~8715.*

Backgrounds

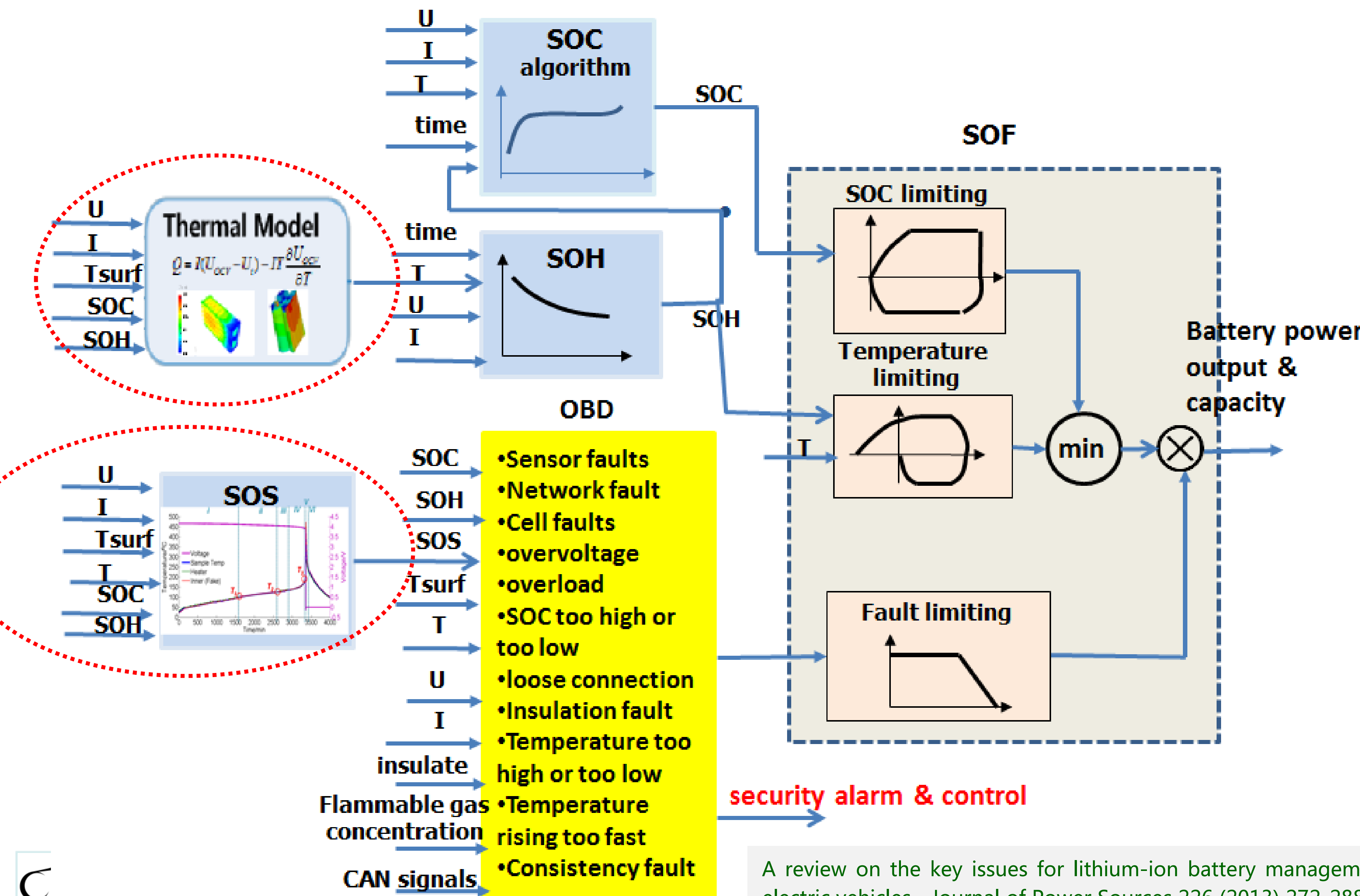








BMS state estimation algorithm framework



A review on the key issues for lithium-ion battery management in electric vehicles , Journal of Power Sources 226 (2013) 272-288

Over heat thermal runaway of EV NCM battery

Xuning Feng , Mou Fang , Xiangming He , Minggao Ouyang*, et al, Thermal runaway features of large format prismatic lithium ion battery using extended volume accelerating rate calorimetry, Journal of Power Sources 255 (2014) 294-301

Motivation

NCM has high specific energy and has been applied in EV, how about the safety?

Object

(1) Investigate the mechanism of the thermal runaway of NCM by using EV-ARC (extended volume accelerating rate calorimetry).

(2) Find the over-temperature SOS (state of safety) for BMS.

The NCM： 25Ah

Fig. 1. The illustration of the es-ARC with double systems made by the THT.

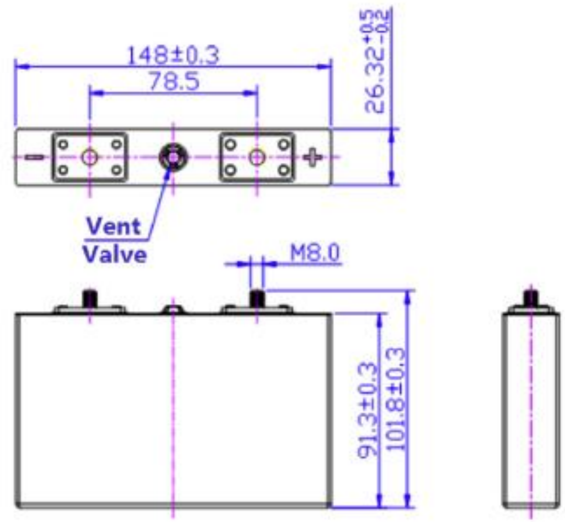
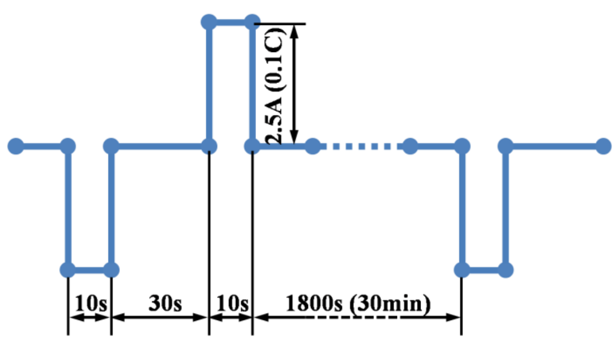


Fig. 2. The product dimensions of the 25 Ah NCM battery.



The pulse charge/discharge profile

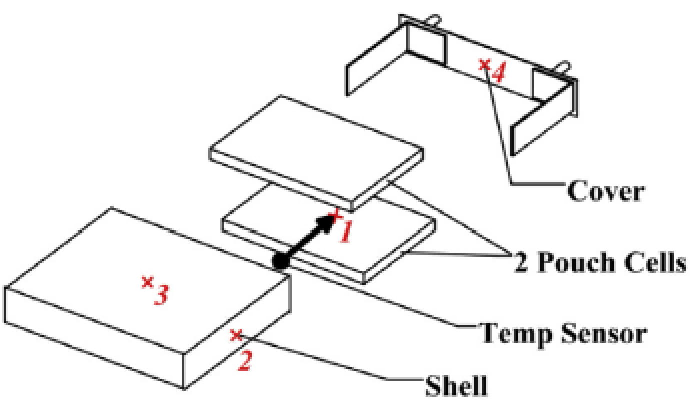
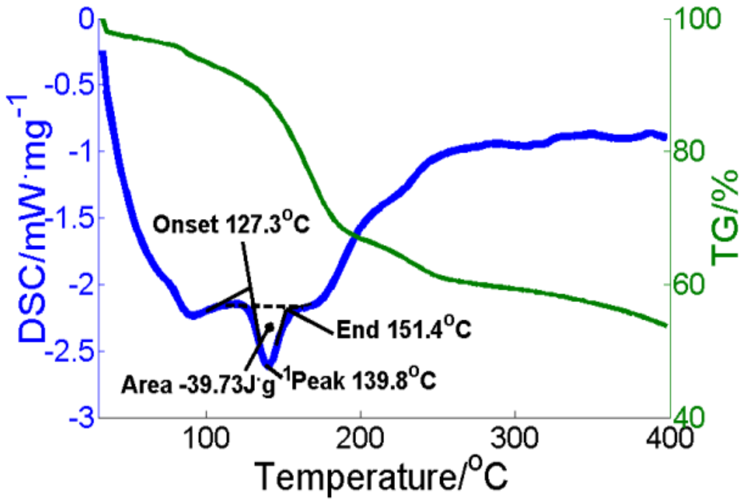


Fig. 4. The positions of the thermocouples.

Test results

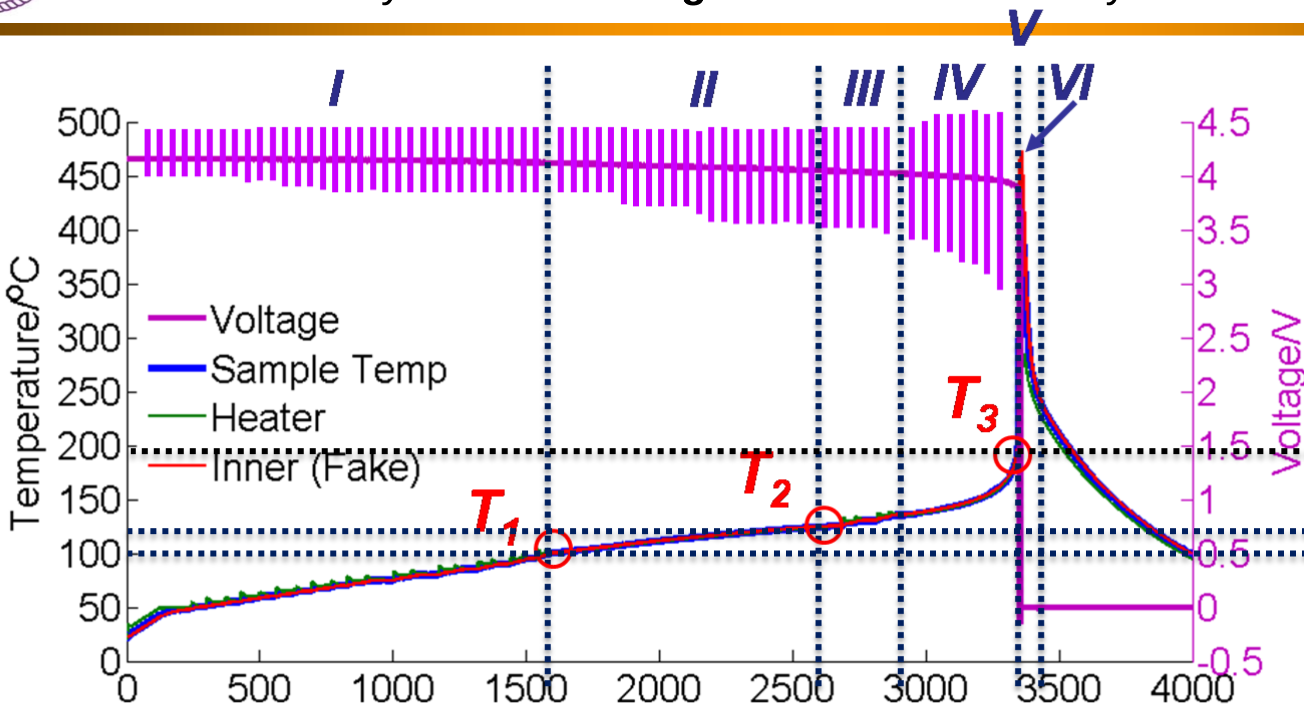
● the DSC/TGA test result of the separator

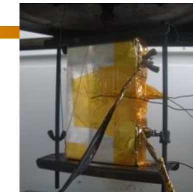
- The endothermic peak locating at 139.8°C with an onset temperature of 127.3°C and an enthalpy of -39.73J·g^{-1}
- The separator with ceramic coating does not lose integrity until about 230°C while the voltage drops sharply indicating a breakdown behavior

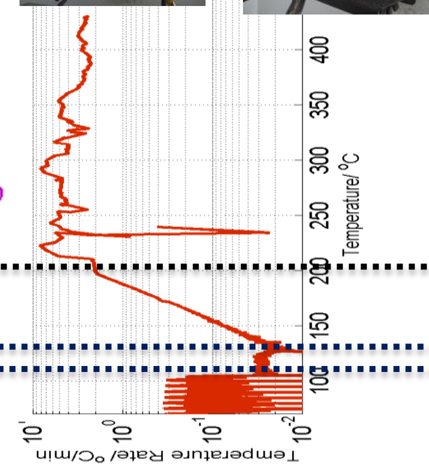


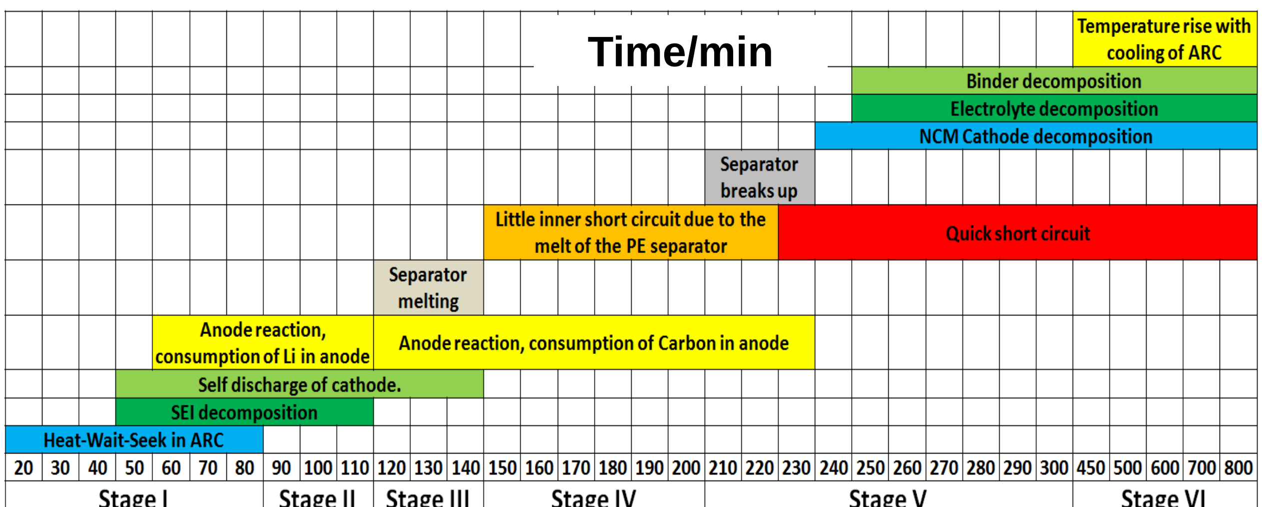
Thermal runaway

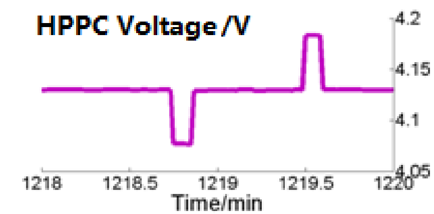
Thermal runaway features of **large format** NCM battery

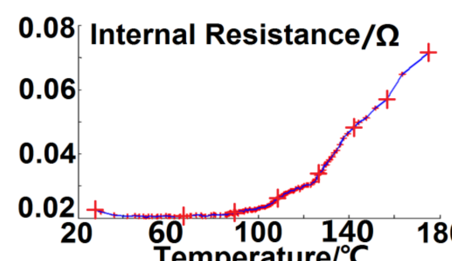






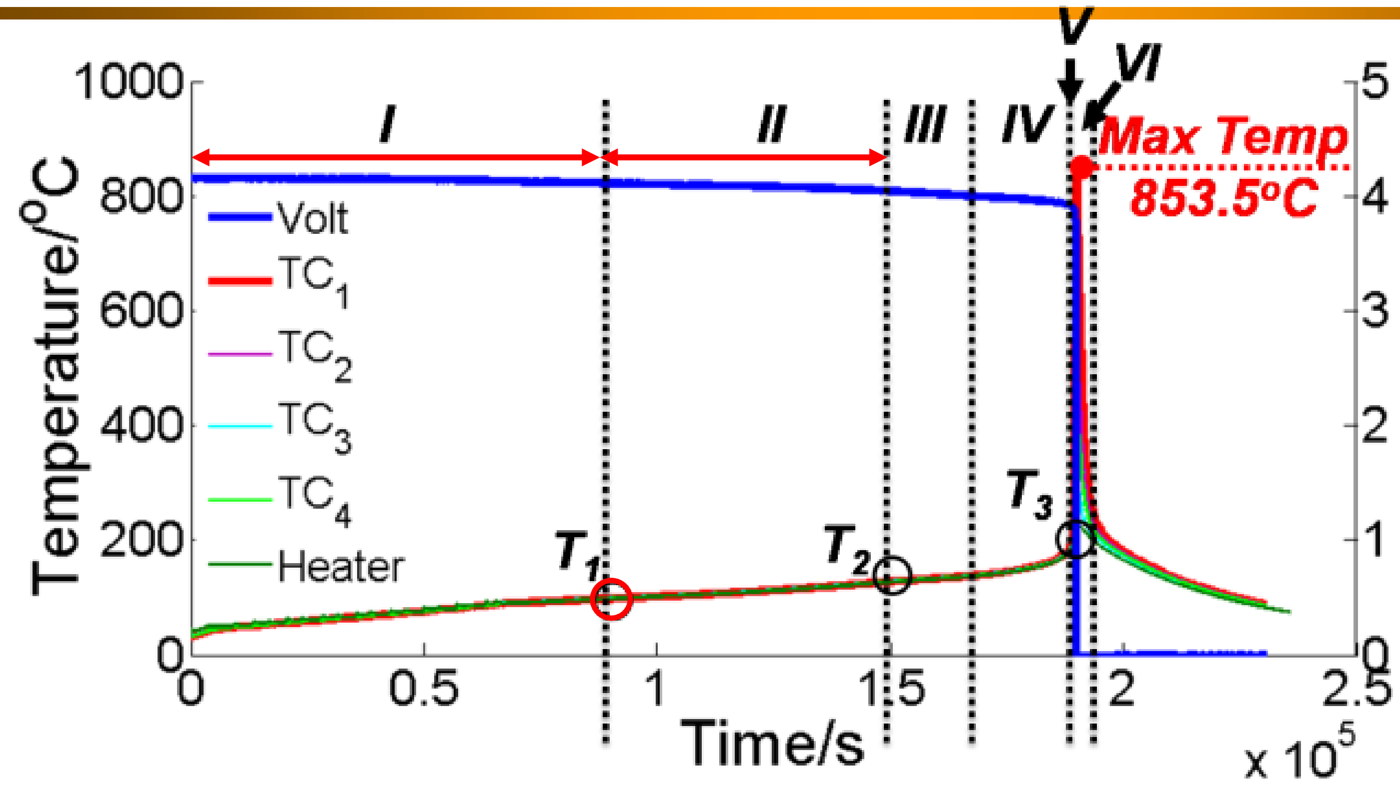


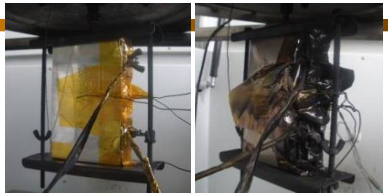


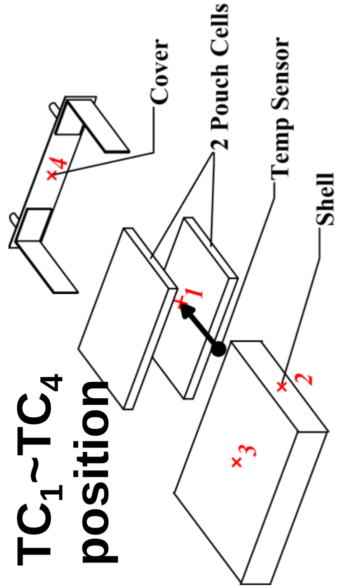


* *X. Feng, X. He, M. Ouyang, et al. J. Power Sources, 2014, 255: 294-301.*

Thermal runaway stages



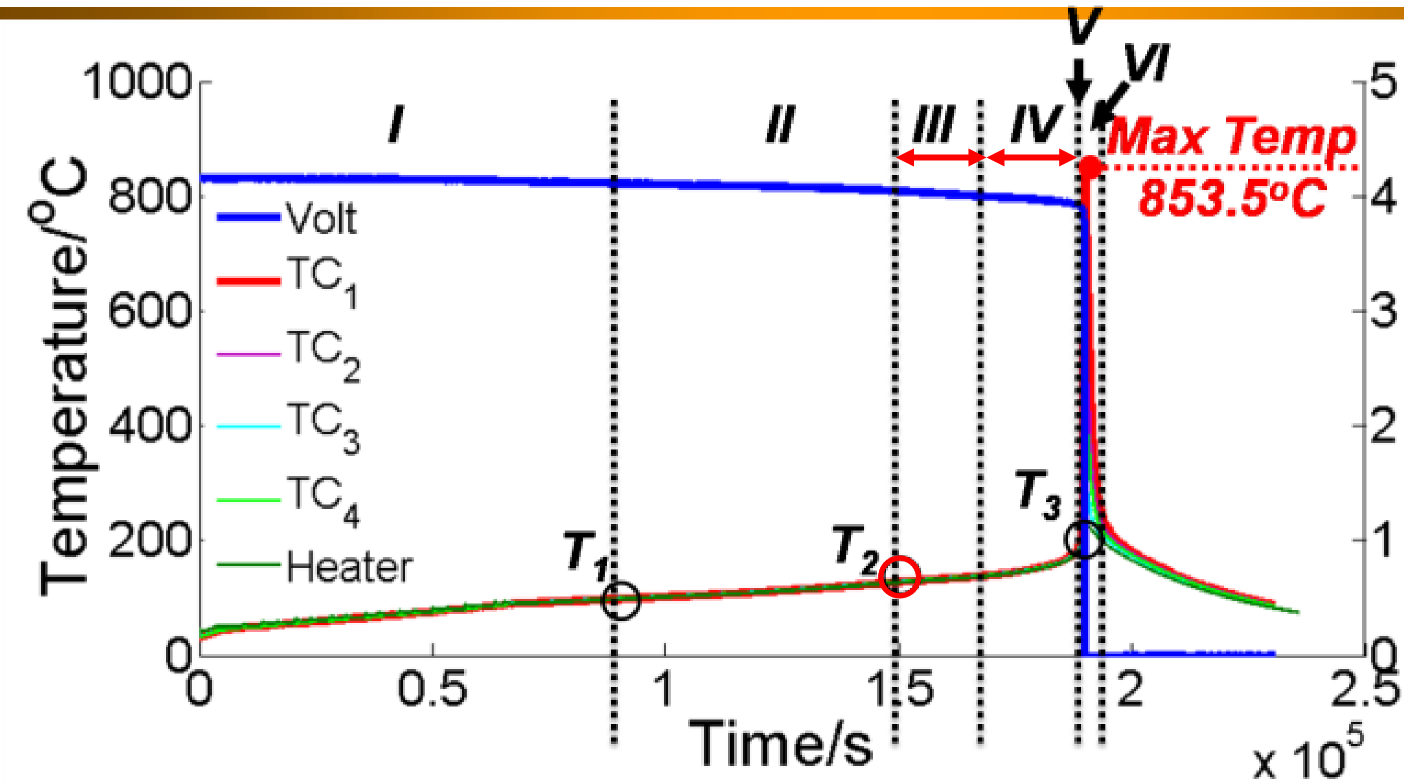


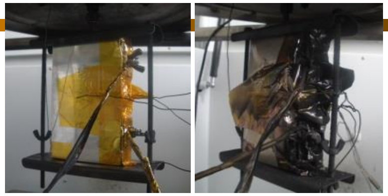


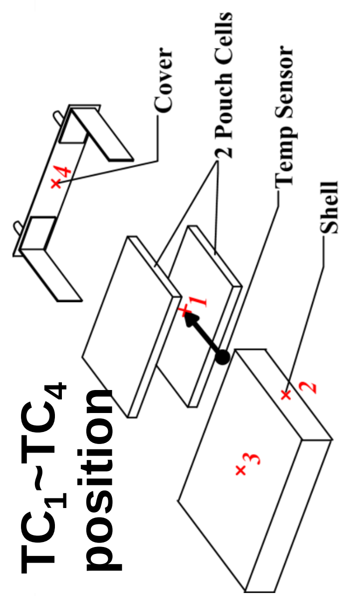
Stage I: The capacity fades at high temperature.

Stage II: T_1 is the onset temperature of detectable **self-heating** and the start temperature of Stage II. In Stage II, the capacity continues fading at higher temperature, the SEI decomposition happens. Losing its protection layer the anode starts to react with the electrolyte and releases detectable heat. **T_1 ≈90°C in this case.**

Thermal runaway stages



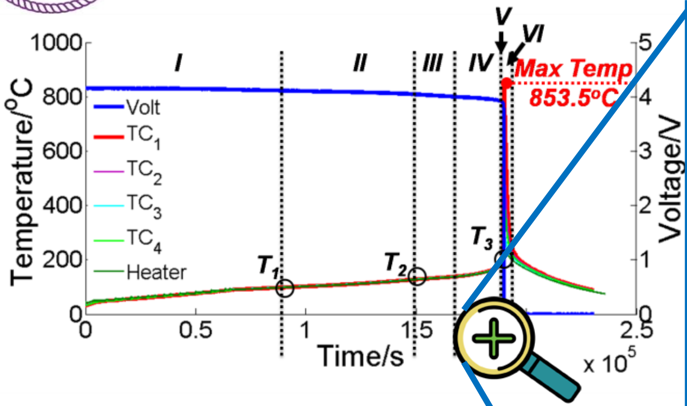




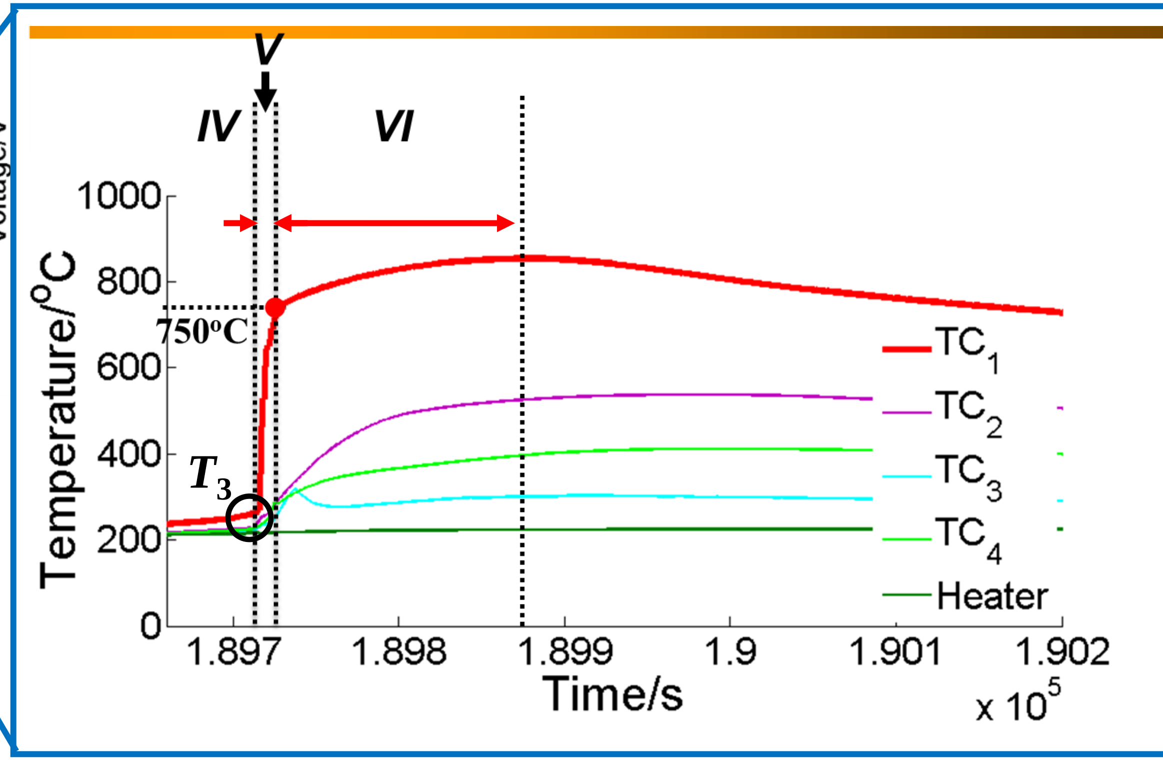
Stage III: T_2 is the start temperature of Stage III, the progress of the temperature rise slows down due to the separator melting. **T_2≈120°C in this case, Stage III ends around 140°C.**

Stage IV: Accelerating process starts with micro short circuit inside. The anode reaction continues consuming active material in the negative electrode. Though in general acknowledgment, the cathode material should have started to react at this stage, the NCM cathode seems to be strong enough not to react until the temperature reaches 240°C or higher.

Thermal runaway stages



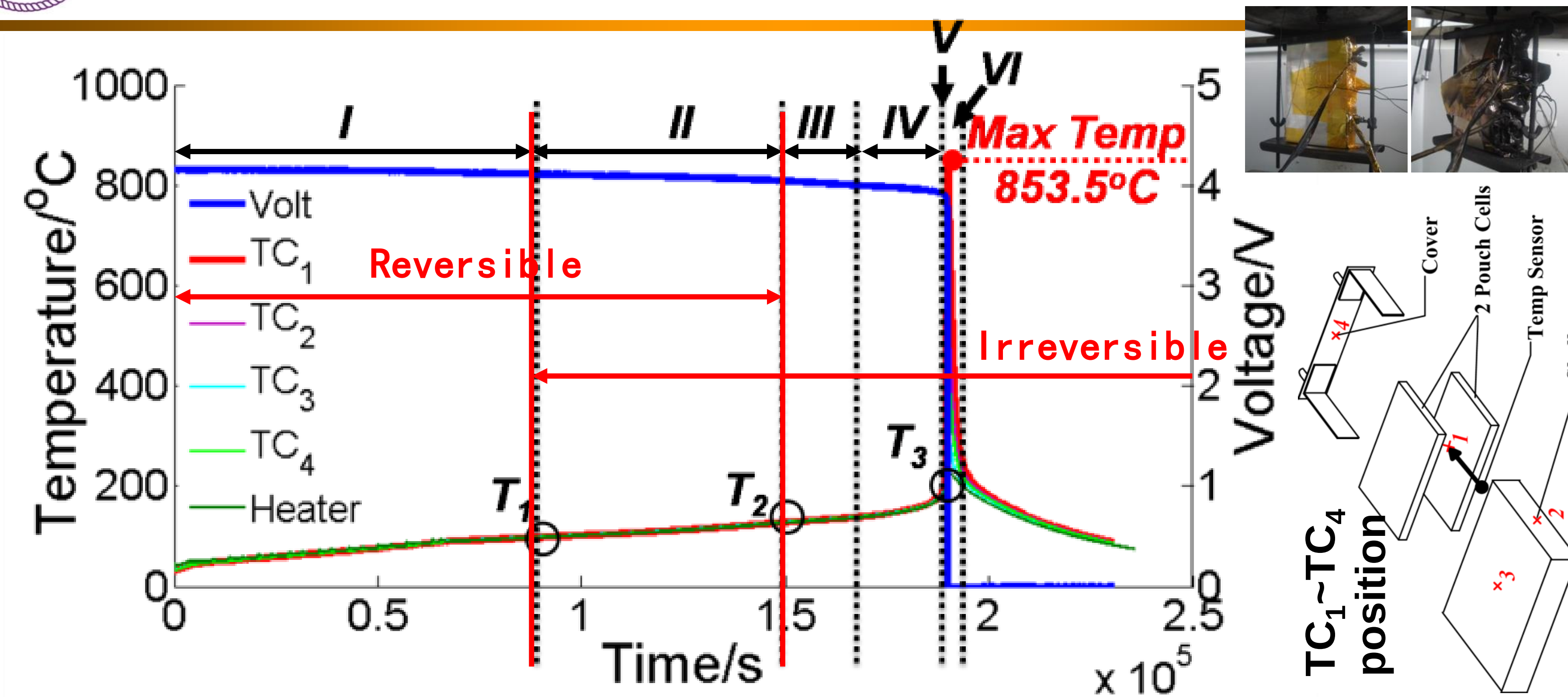
Magnify the figure to explain Stage V&VI.



Stage V: T_3 is the start temperature of Stage V, when the temperature starts to go up exponentially. In the Stage V, the separator loses its whole integrity, fierce short circuit occurs, reactions such as the NCM cathode decomposition, electrolyte decomposition, and PVDF decomposition, happens, and energy releases instantly.

Stage VI: Residual reactions continue bringing the temperature a little higher, from about 750°C to the maximum. The temperature rate is much lower than that in Stage V.

Thermal runaway stages



Reversible control limit:

Before the temperature reaches T_2, the battery maintains more than 70% reversible capacity.

The melting of separator:

In this case the separator starts to melt at about 120°C. After that the battery can not release energy due to the characteristic change of the separator.

Irreversible capacity loss:

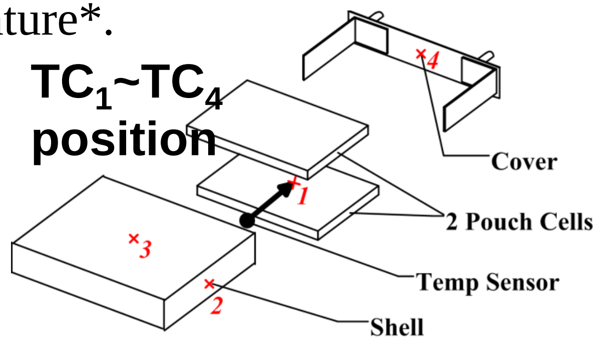
Obvious irreversible capacity loss starts at around T_1. Active material of the battery decays in high temperature.

Temperature difference within the battery

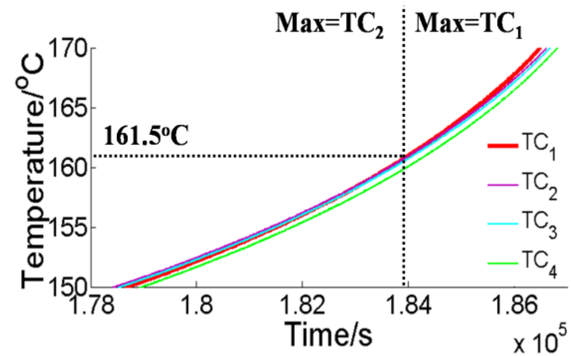
- For thermal runaway triggered by an internal short circuit, the maximum temperature difference is as high as approximate 600°C from some literature*.

- TC_1~TC_4 are used to analyze the temperature distribution within the battery during the test.

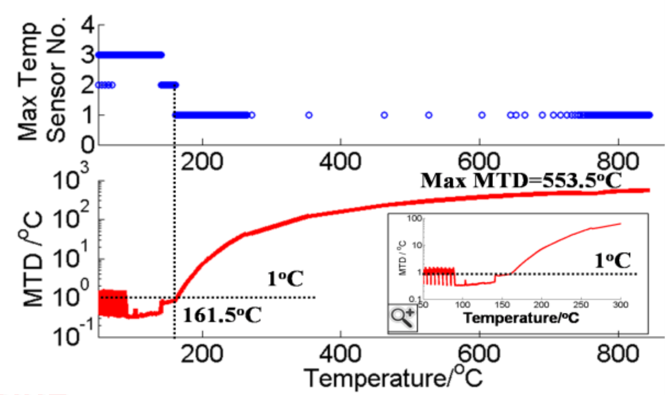
TC_1~TC_4 position



- The temperature difference among the 4 thermocouples is quite small during most time of the self-heating process.
- The maximum temperature difference (*MTD*) is not as high as 1°C until the temperature reaches 161.5°C, which takes about 184000s (51.1hrs).



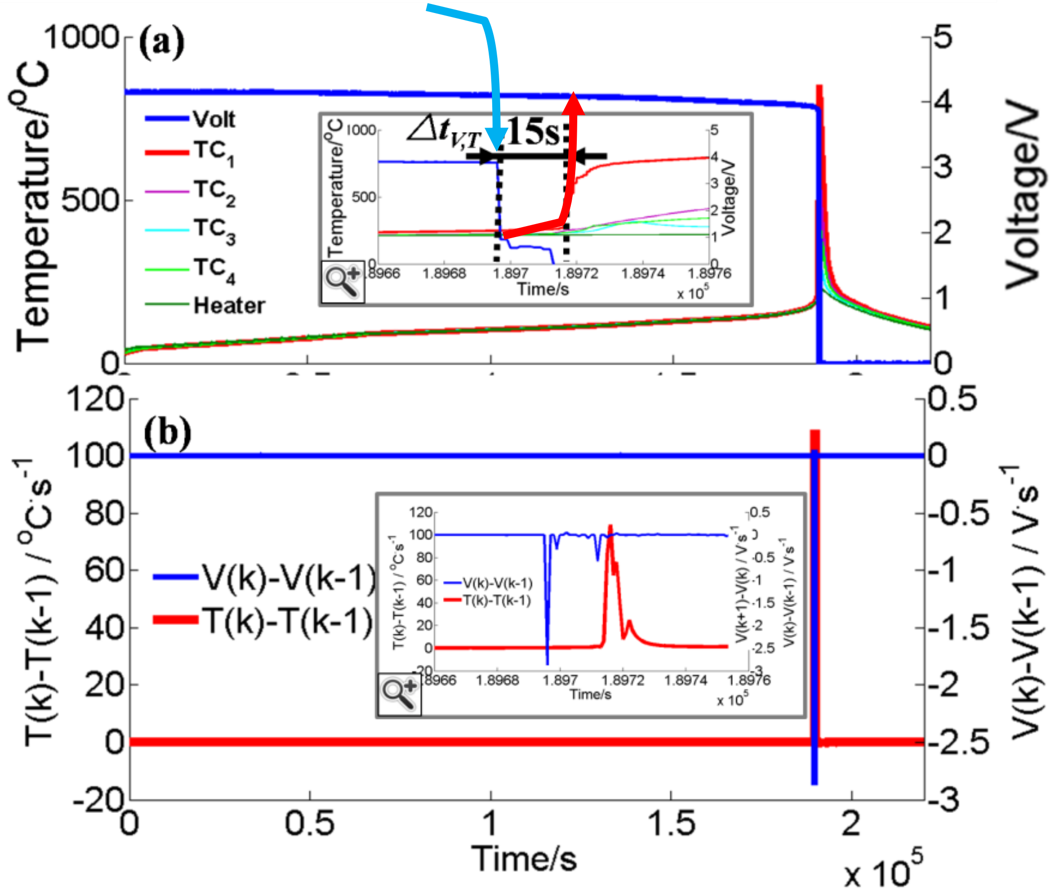
- As the thermal runway occurs at about 190000s, it means that the *MTD* maintains lower than 1°C for 184000/190000=97% of the whole test.
- What's more, from that point the temperature of TC_1 starts to take the lead and rise much faster than the others do.



*G.H. Kim et al.. J. Power Sources. 2007, 170: 476-489.

Interval between V drop & T rise

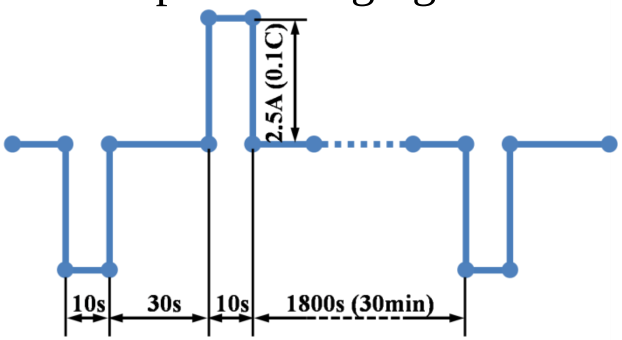
- During the experiment, it is observed that the sharp drop of the voltage occurred a little sooner than the instantaneous rise of the temperature. The time between V drop and T rise is about **15s**.

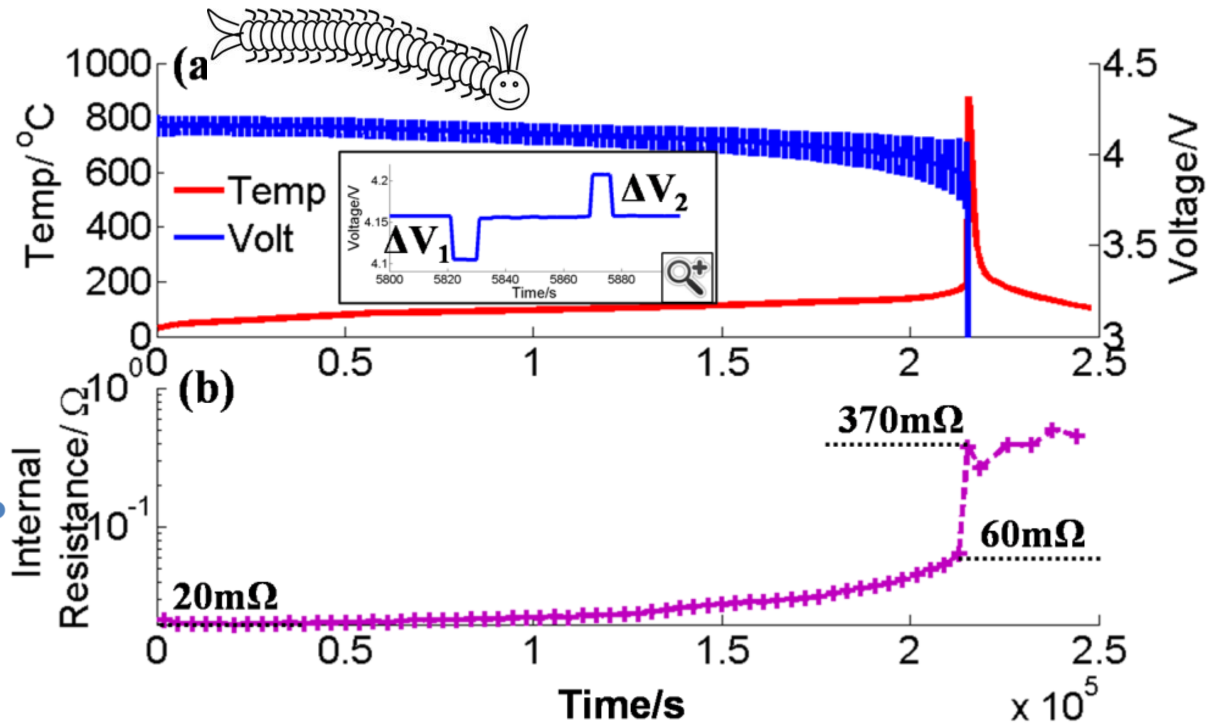


- **The interval between the voltage drop and the temperature rise provides a possible way to predict the occurrence of the coming thermal runaway. That is the last chance for the BMS to inform the driver that the battery is very dangerous.**

The variation of the internal resistance

- The variation regulation of the internal resistance during the thermal runaway test has been studied using a test profile with pulse charging.





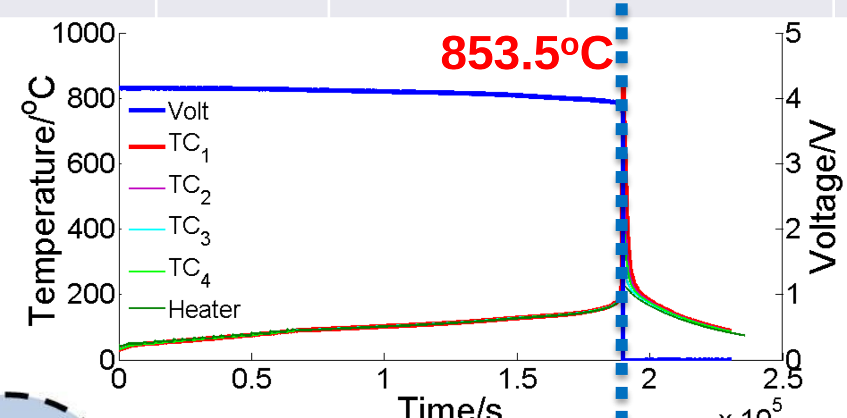
- The millipede-like voltage curve employs many discharge/charge periods. The voltage pulse of discharge is ΔV_1, the voltage pulse of charge is ΔV_2 and the pulse current is ΔI=2.5A.
- The internal resistance R_{in} is defined as the quotient of the average pulse voltage and the pulse current: $$R_{in}= (\Delta V_1+\Delta V_2)/2\Delta I$$
- The initial R_{in} is 20mΩ. Then the R_{in} rises slowly to 60mΩ before the thermal runaway happens. At around 250°C, the separator loses its integrity, so that the thermal runaway happens due to massive internal short circuit. Correspondingly, the battery swells and R_{in} rises to 370 mΩ.

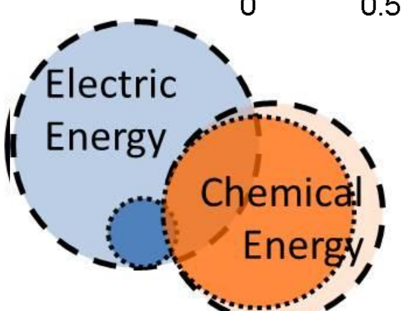
The enthalpy of thermal runaway

- From the maximum internal temperature, we can make:

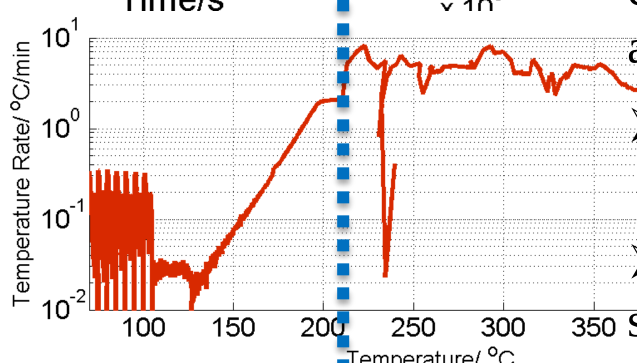
A definition of enthalpy: $\Delta H_{total}=\Delta T*M*Cp=(853.5-90)*0.720*1100=604692J$

Reaction	SEI Dec.	Anode Dec.	Cathode Dec.	PVDF Dec.	Electrolyte	Short Energy ΔH	Total J
Entropy/(Jg^{-1})	257	1714	161	1500	285	3.8V	Chemical
Mass/g	15.09	100.58	179.12	24.14	108	25Ah	272,100
Total Energy/J	3878	172394	28838	36210	30780	342000	+
Reaction Onset/°C	70	110	170	240	250	250~260	*614100*





0% SOC battery



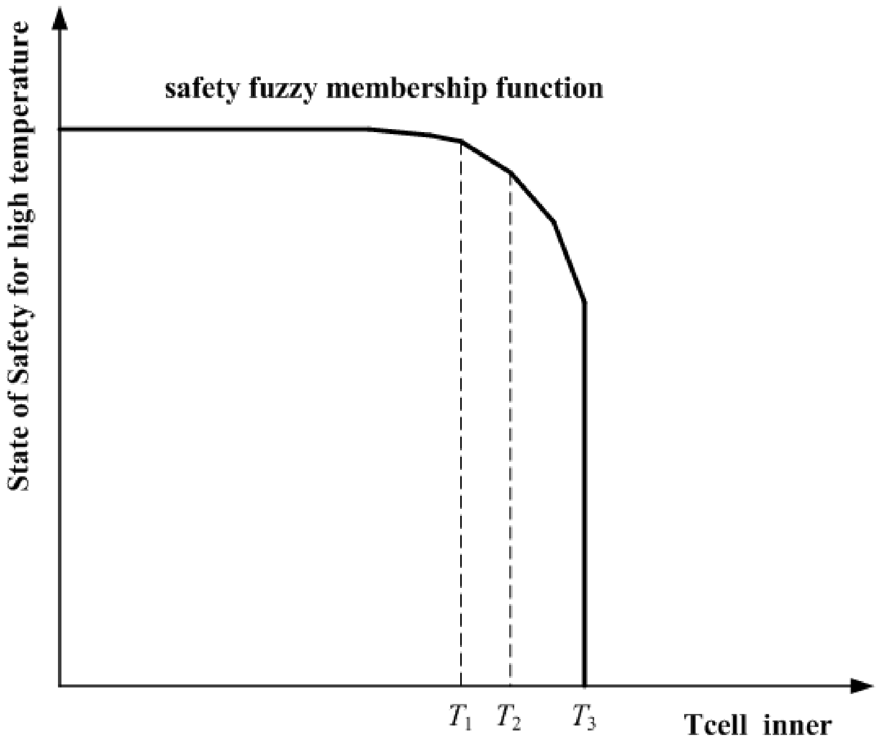
- The total energy (ΔH_{total}) should include Electric and Chemical Energy.
- The total chemical energy (E_c) can be got from literature. (**~272100J**)
- The electric energy (E_e) can be calculated by multiplying the voltage and the capacity. (**~342000J**)
- The E_c and E_e have intersections:
  Here **614100-604692=9408J**
- The area of E_c and E_e will both shrink when the battery is discharged.

Conclusion

- ✓ Three key temperatures, T_1 (90℃) , T_2 (120℃) and T_3 (230℃). Obvious irreversible capacity loss starts at around T_1. After the temperature reaches T_2, it loses most of its capacity, T_2 might be an upper limit for the safety management. After T_3, thermal runaway cannot be extinguished at that time.
- ✓ The separator with ceramic coating is more safe for large battery, it does not lose integrity until about 230 ℃ until the voltage drops sharply indicating a breakdown behavior.
- ✓ The internal resistance increases slowly from 20mΩ to 60mΩ before thermal runaway (separator shut down is not work good at large battery) . When thermal runaway happens, the internal resistance rises to 370mΩ indicating the loss of integrity of the separator or the swell of the pouch cells.
- ✓ The temperature difference within the battery stays lower than 1ºC for most of the test time. The temperature difference increases as the test goes on, and it rises to its highest (about 520ºC) when thermal runaway happens.
- ✓ The time interval between the sharp shutdown of the voltage and the exponential rise of the temperature is observed. It takes about 15~40s from the voltage drop to the temperature rise. Such a time interval is good for a possible early warning of the battery thermal runaway.

Future Work

- **Build a model for battery thermal runaway.**
- **Use that model to evaluate State of Safety, before the temperature of the battery reaches T_2.**
- **Propose feasible algorithm for the BMS to evaluate the State of Safety for Li-ion battery.**
- **Employ the enthalpy results to analyze the thermal runaway propagation process.**



Over charge safety of EV NCM battery

Results will be submitted to JPS.

- **Motivation**

NCM has high specific energy and has been applied in EV, how about the over-charge safety?

- **Object**

(1) Investigate the mechanism of over-charge thermal runaway of NCM.

(2) Find the over-charge SOS (state of safety) for BMS.

Test cell

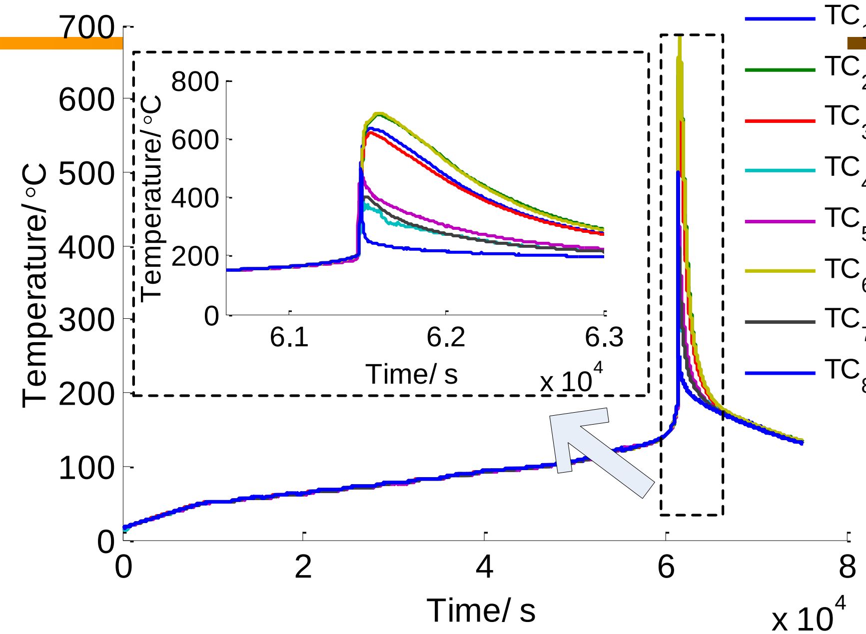
Test cell parameters

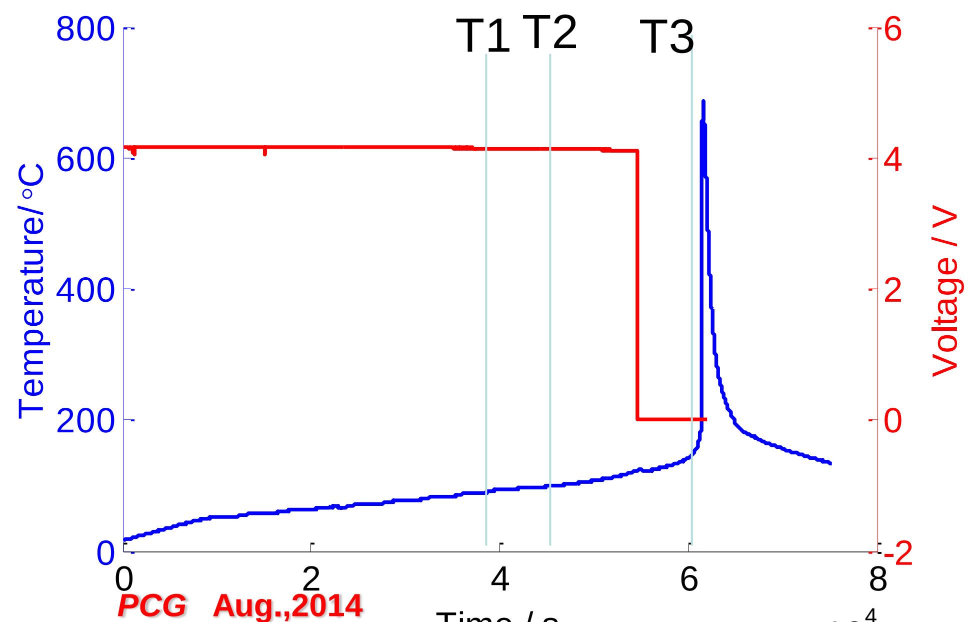
items	values
weight	500±5g
Rated voltage	3.7V
Rated capacity	20Ah
Charging Cut-off voltage	4.2V
Discharging cut-off voltage	2.5V
Charging current	Standard charging:10A(0.5C) Quick charging :20A(1.0C)
Full charging time	Standard charging:2.5h Quick charging :1.5h
Maximum charging current	20A(1C)
Maximum discharging current	60A(3C)

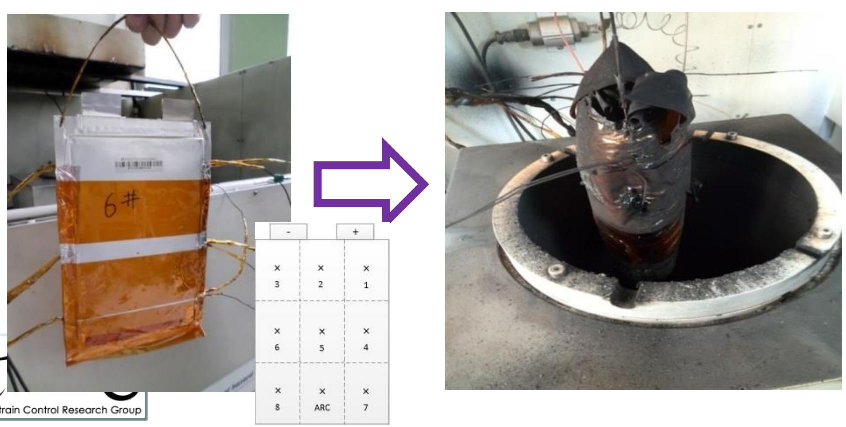
Pouch cell

ARC over-temperature thermal runaway test

- The self heating temperature T1 is about 90°C, and the separator melt temperature T2 is about 120°C, the thermal runaway temperature T3 is 190°C , the maximum temperature is 680.36°C ;
- After the thermal runaway, the battery weight reduces 41.26% (from 991.06g to 582.11g) ;
- The battery were expanded seriously and rupture. All the cathode and separator material were ashed, the anode was deformed seriously and material was flake off from Cu current collector.

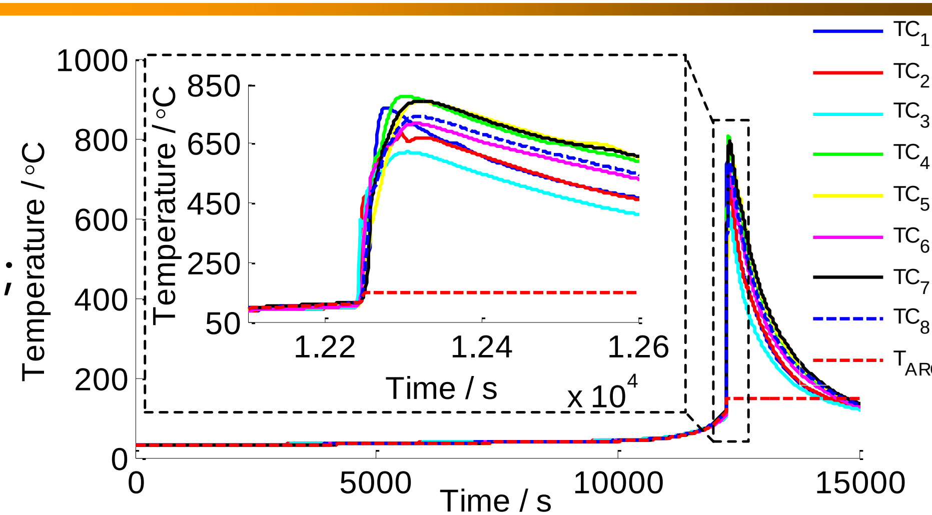


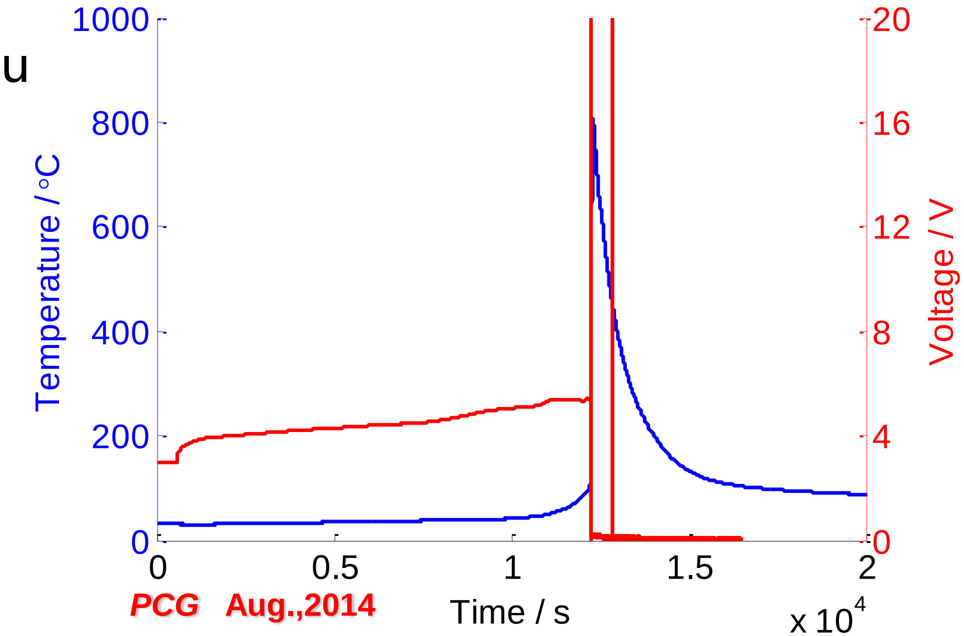




ARC over charging thermal runaway test

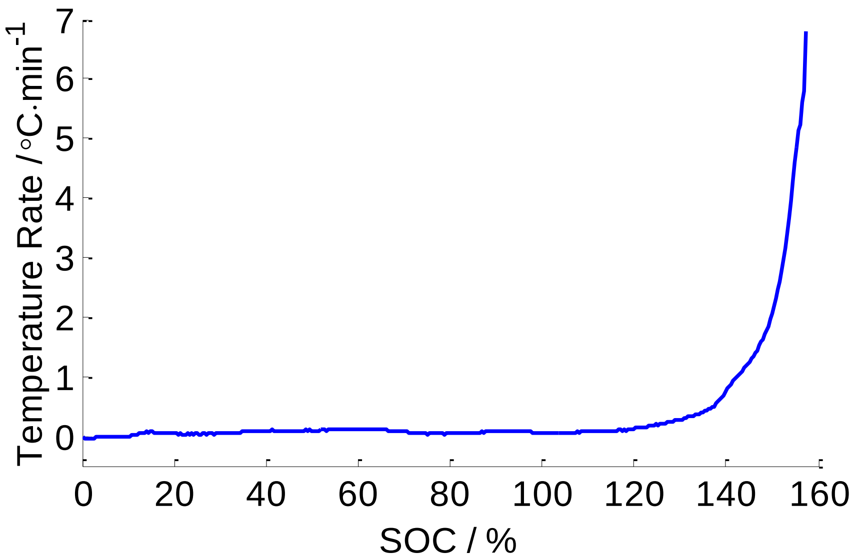
- The overcharging thermal runaway temperature is 110°C , the maximum temperature is 808.36°C ;
- The time between the OCV dropping and the thermal runaway is about 9s ;
- After thermal runaway the battery weight reduced 53% (from 991.06g , to 465.81g) ;
- The battery were expanded seriously and rupture. All the cathode and separator material were ashed, the anode material was flake off from Cu current collector (especially in the middle). Some Cu current collector were melt and broken).

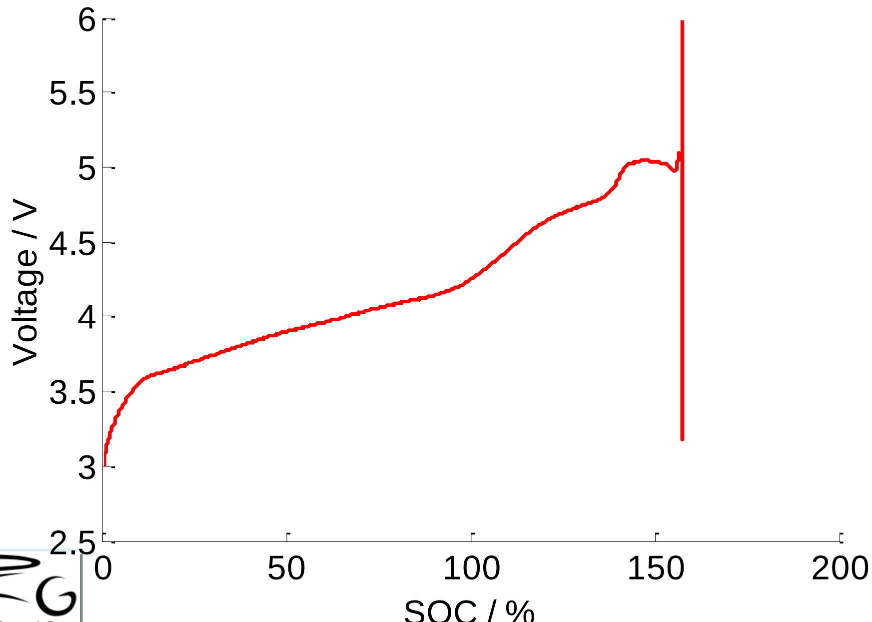


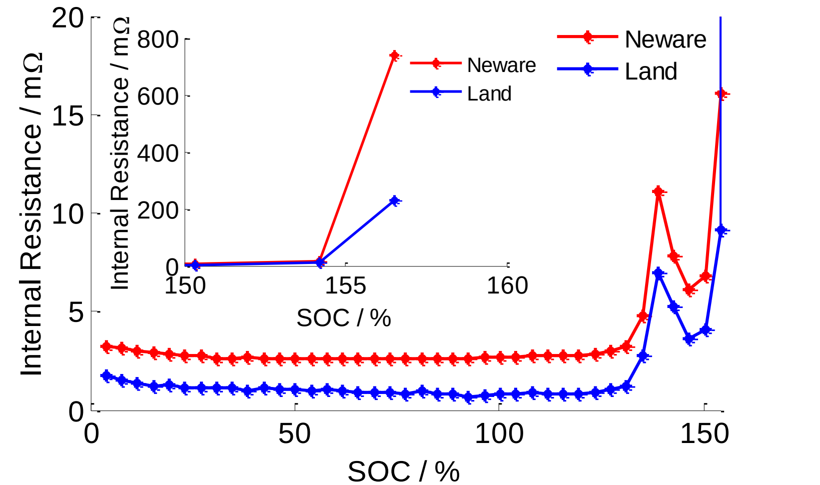


ARC over charging thermal runaway test

- After SOC>120%，the temperature rate increase exponentially.
- SOC=144.8~152.1%，there is a 5V platform；
- SOC≅130%，the battery resistance increased to a peak at SOC=138.8%；then it dropping to a bottom at SOC=146.5%, then rise up quickly to 201.4 mΩ just before the thermal runaway happen.



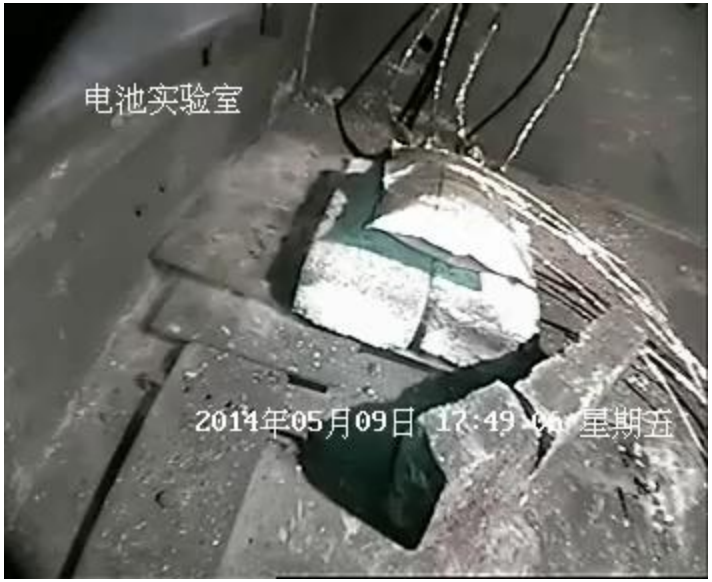


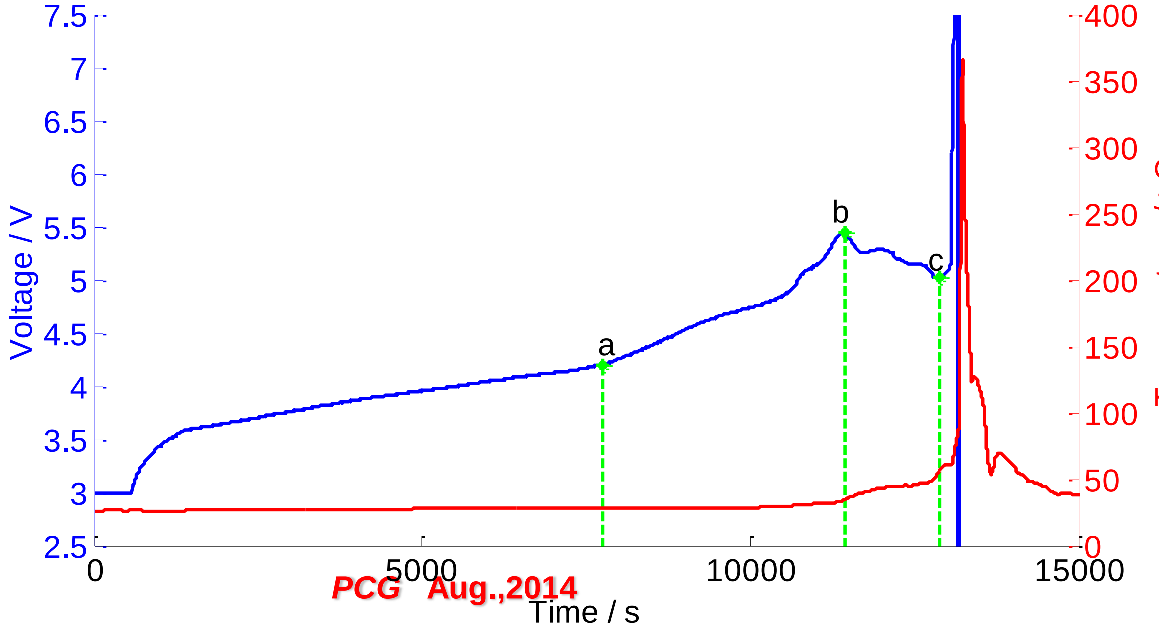


PCG Aug.,2014

over charging thermal runaway test under room temperature

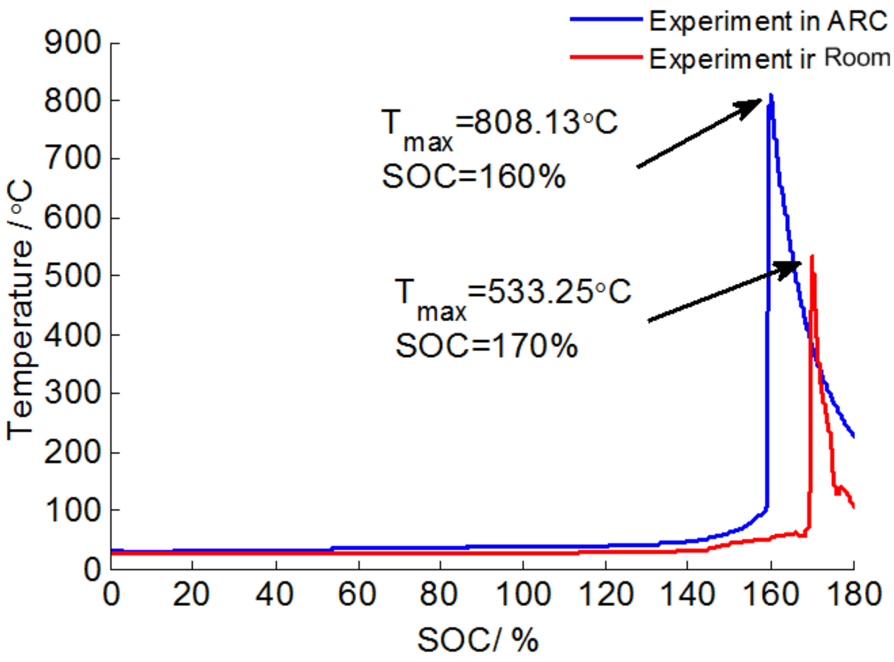
- The battery begins swell after the voltage reach the peak point b and there is a platform 5.1~5.2V.
- The battery is cracking at the point C because of the high internal pressure, then the flammable gas catch fire.
- The battery got thermal runaway after the serious short circuit caused by the broken of the separator because of high temperature.

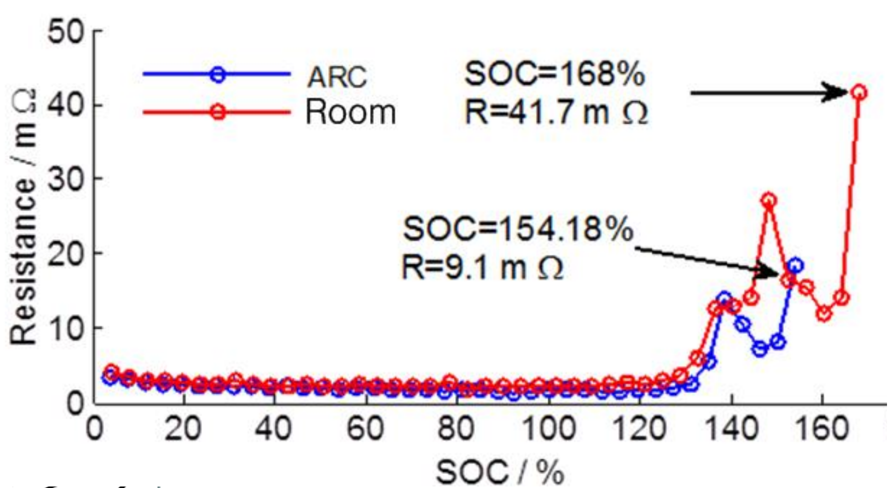


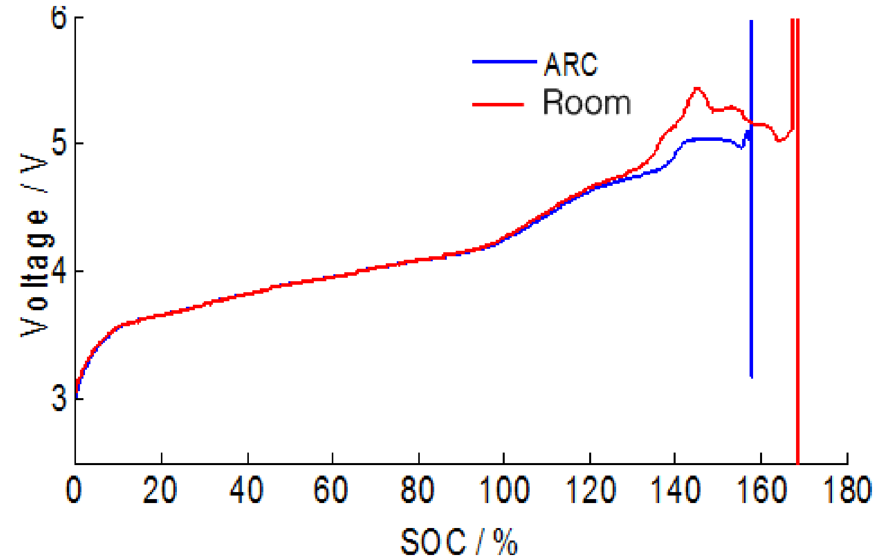


Compare of the thermal runaway at adiabatic (ARC) and under room temperature

- **The battery got thermal runaway more early (about 10% SOC) at adiabatic overcharging than that at room temperature.**
- **The maximum temperature at ARC is larger than that at room.**
- **The two charging voltages are almost the same before SOC 120%. After SOC>120%, the voltage at room temperature is higher.**

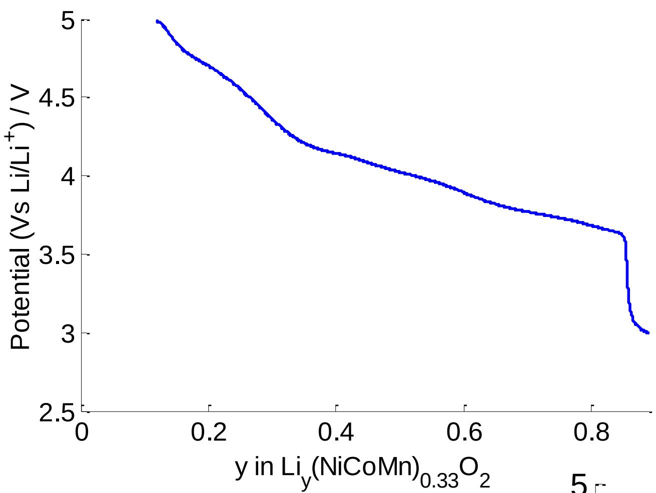




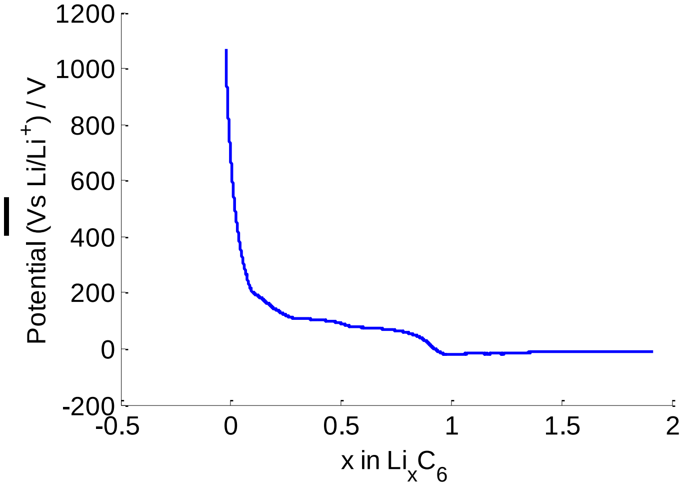


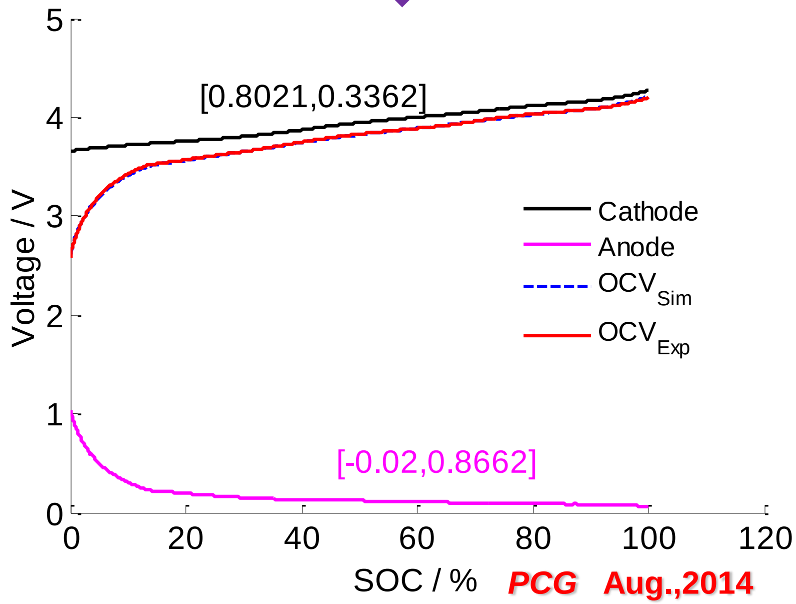
Over charging modeling

Re-construct the battery full cell voltage with anode and cathode half cell potential using genetic algorithm (GA)



Cathode potential – anode potential

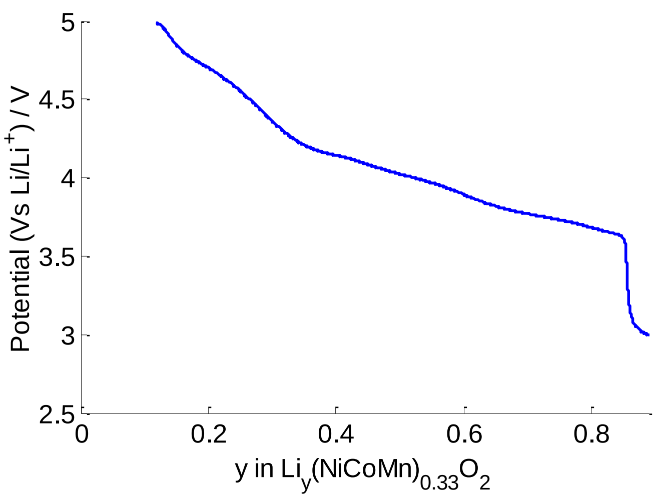




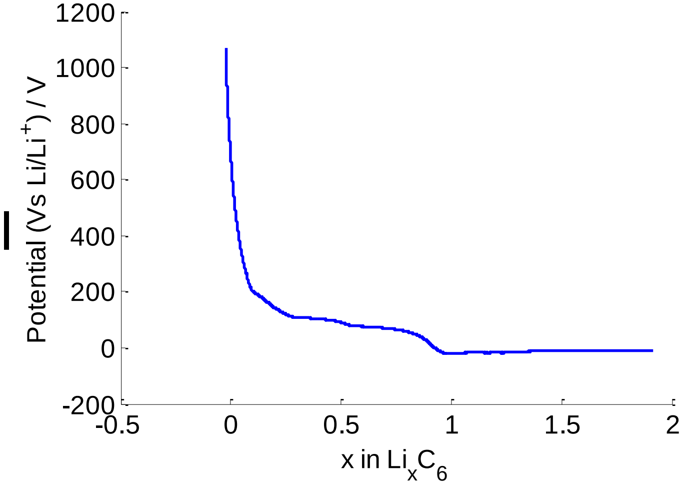
Y. Zheng, L. Lu, X. Han, et al. LiFePO4 battery pack capacity estimation for electric vehicles based on charging cell voltage curve transformation[J]. Journal of Power Sources, 2013, 226: 33-41.

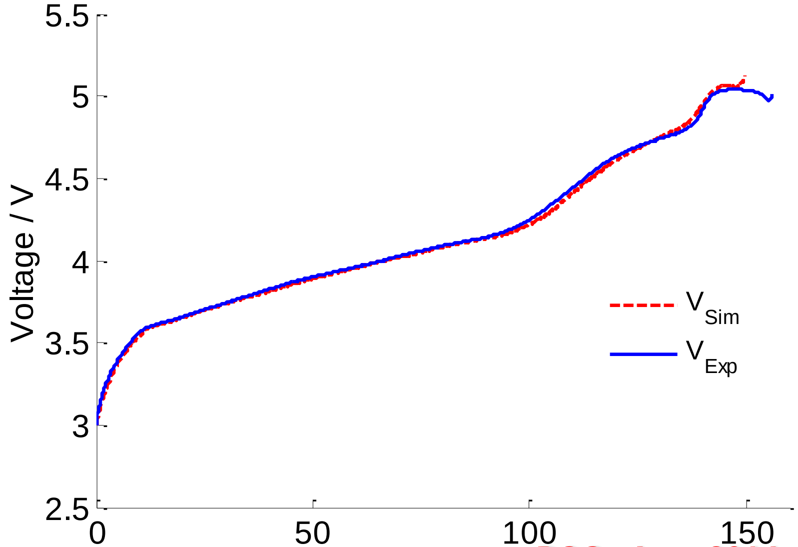
Over charging modeling

Re-construct the battery full cell voltage with anode and cathode half cell potential using genetic algorithm (GA)



Cathode potential – anode potential





Lithium content change

cathode：

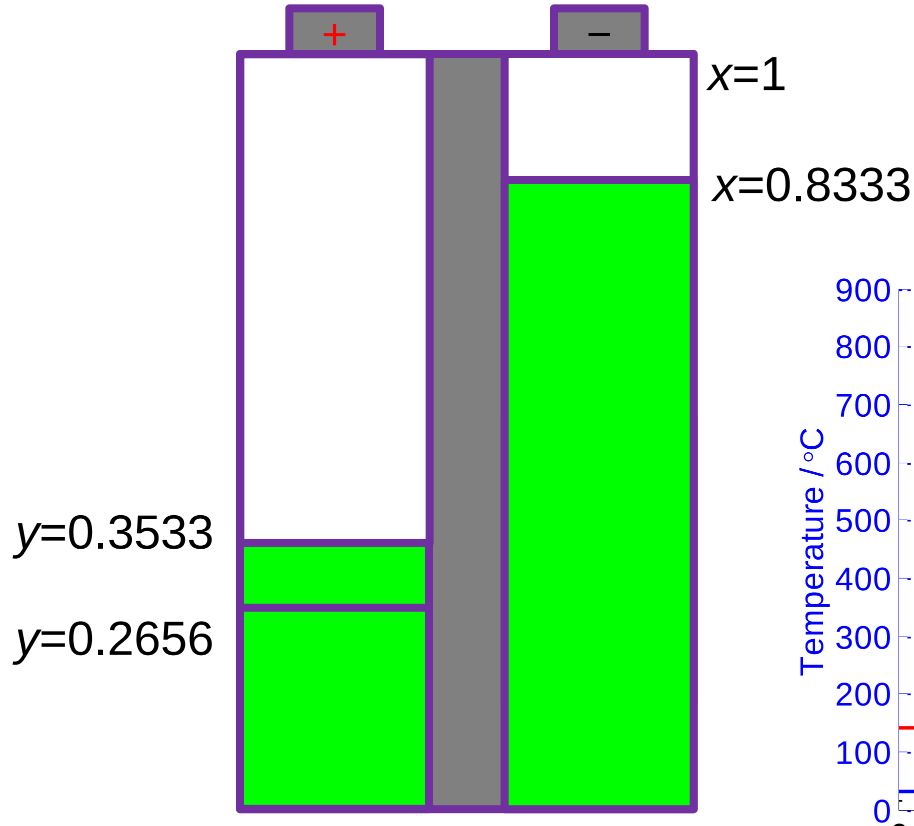
y=0.7950- 0.4417·SOC

anode：

x= 0.8400·SOC-0.0067

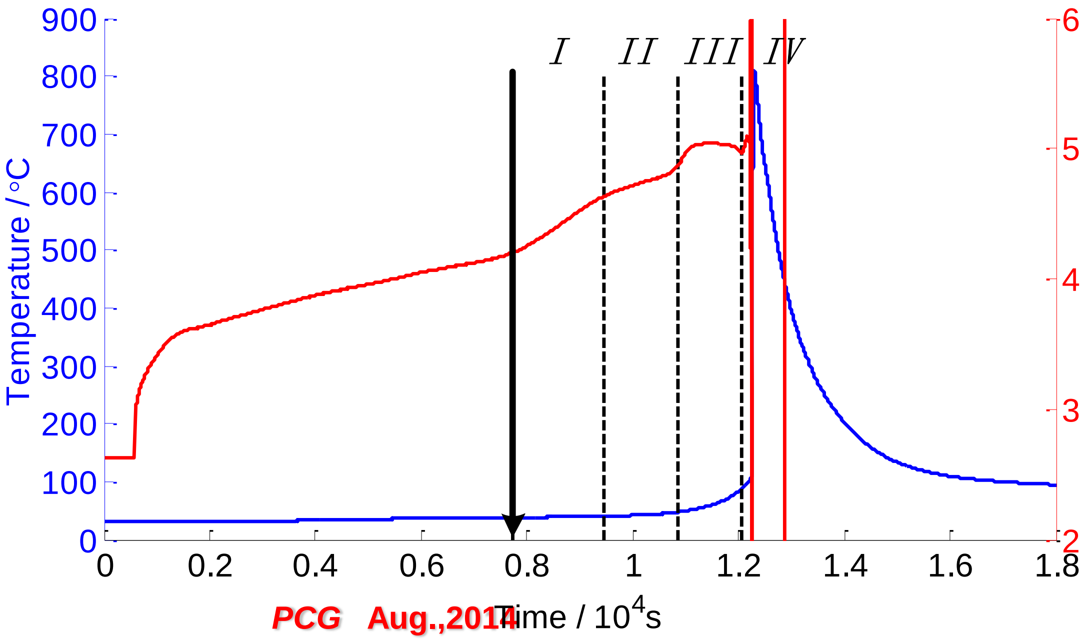
Y. Zheng, L. Lu, X. Han, et al. LiFePO4 battery pack capacity estimation for electric vehicles based on charging cell voltage curve transformation[J]. Journal of Power Sources, 2013, 226: 33-41.

Overcharging process



stage Ⅰ

- Reversible extraction and insertion of lithium ions
- Battery has not yet irreversible structure changes
- Resistance and temperature almost no change.

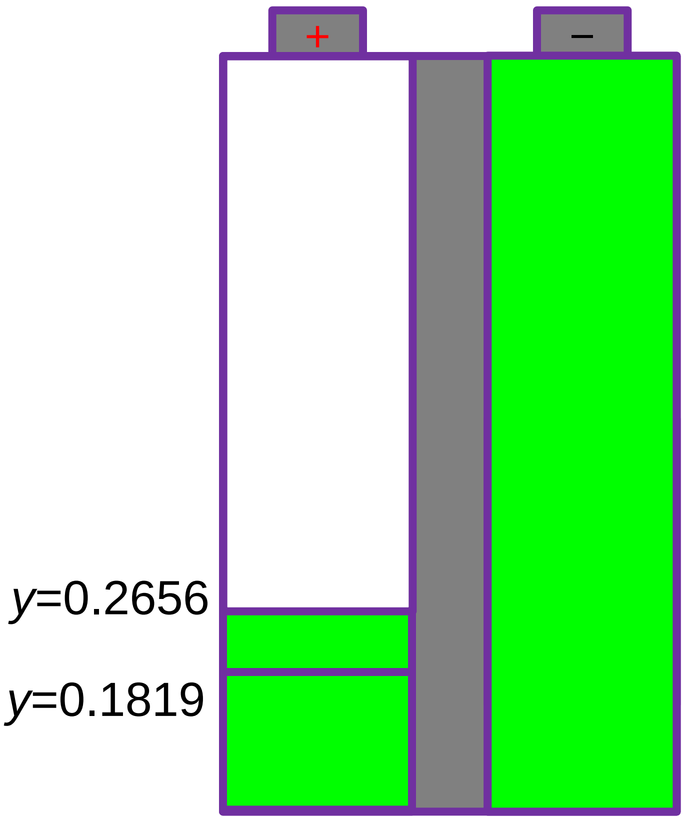


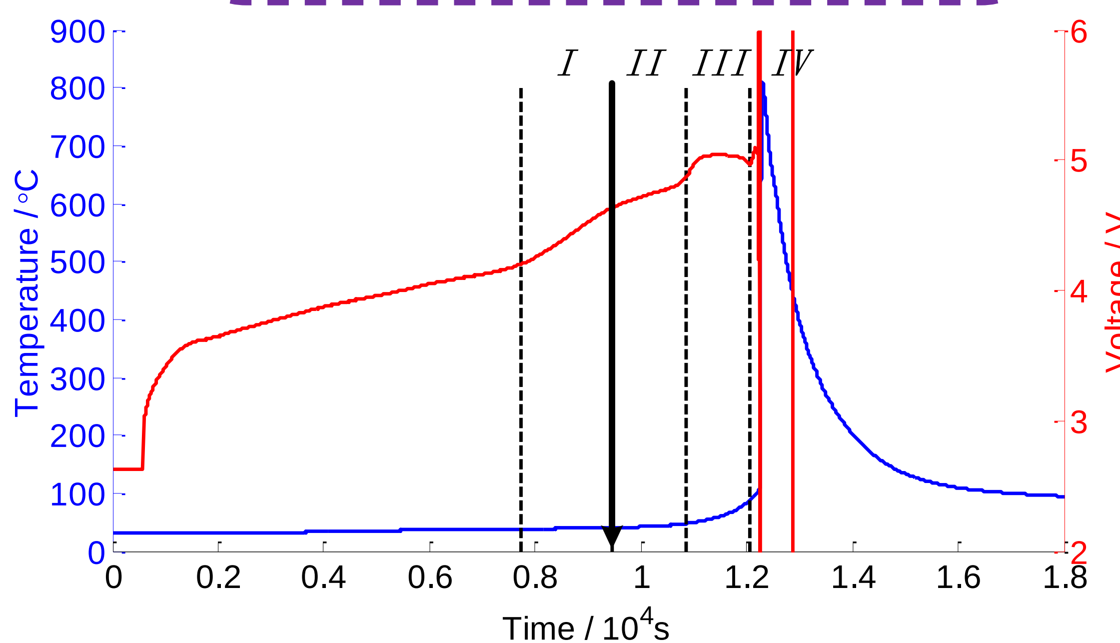
Overcharging process

SOC=120~138.8%
V=4.63~4.90V

stage *II*

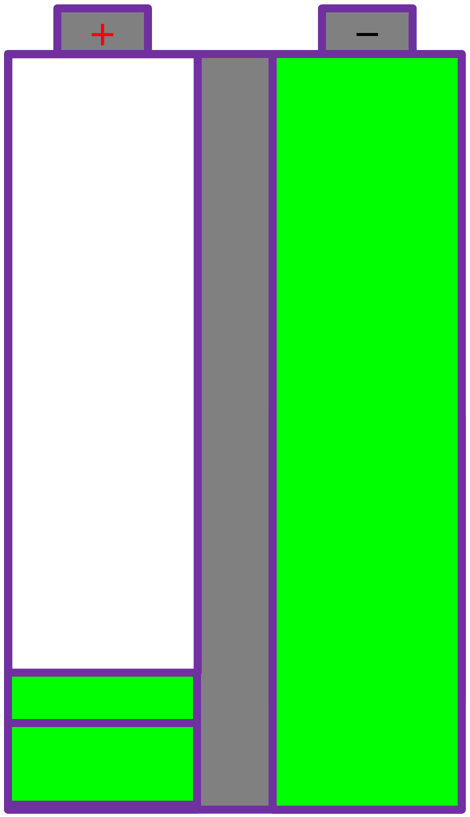
- lithium metal would be deposited on the graphite anode
- The temperature rate is rising
- The structure of cathode is changing
- The resistance is rising quickly.





Overcharging process

SOC=138.8~155.5%
V≈5V

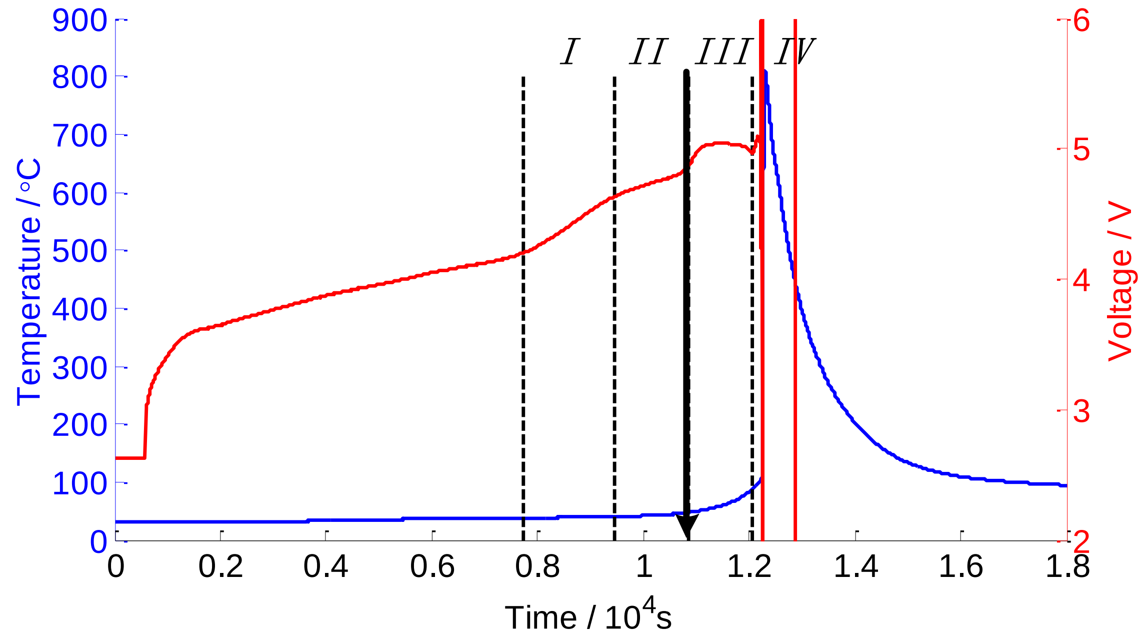


y=0.1819

y=0.1081

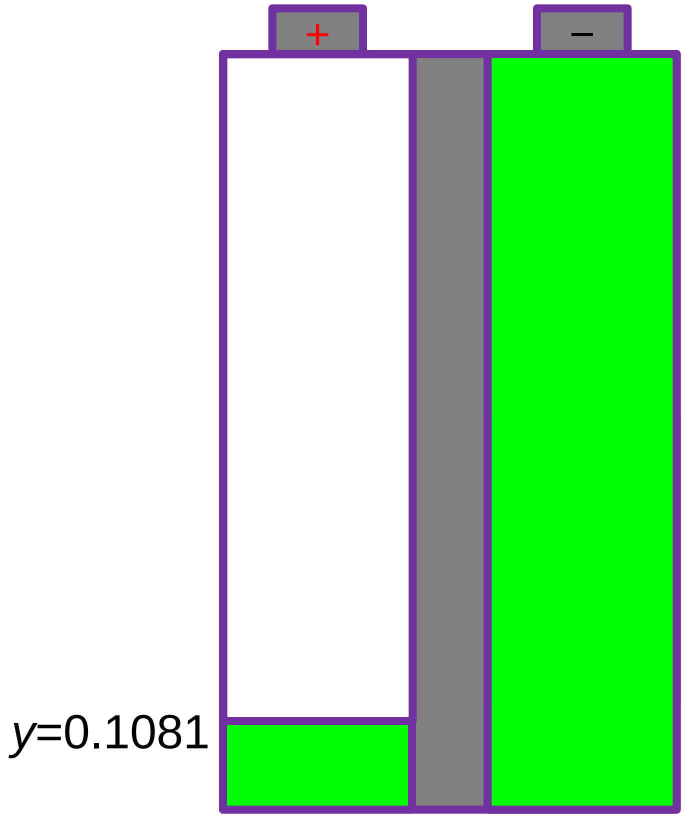
stage *III*

- The electrolyte is oxidized and decomposed , generating a lot of heat and flammable gases
- Temperature rise up quickly
- Battery swell seriously



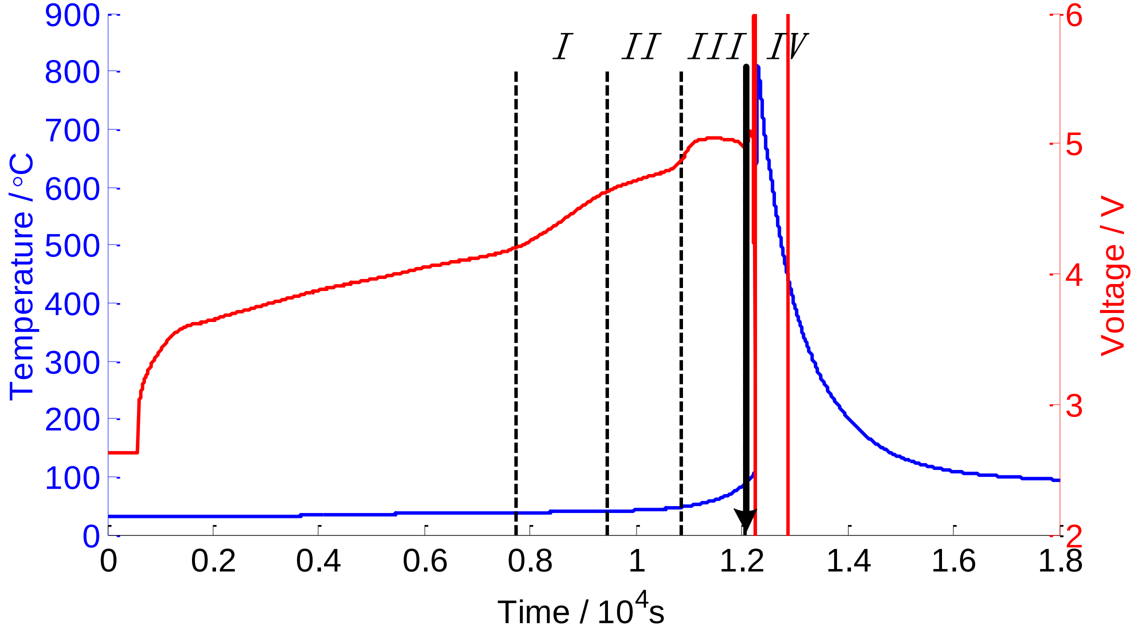
Overcharging process

SOC>155.5%
V>4.97V



Stage *IV*

- voltage rise up quickly to the charger limited.
- Battery rupture.
- Seriously short circuit and thermal runaway.



Powertrain Control Research Group

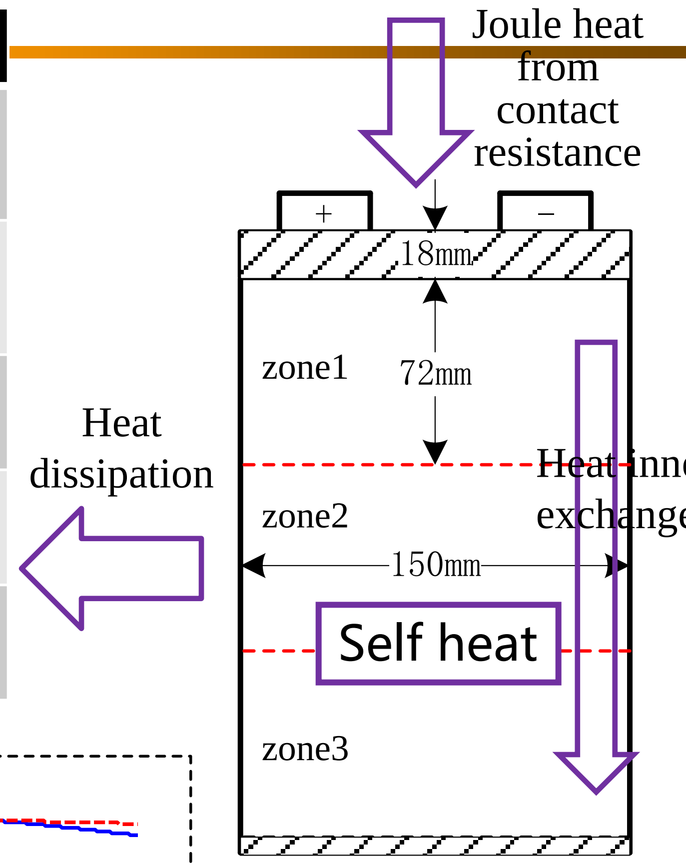
Overcharging thermal modeling

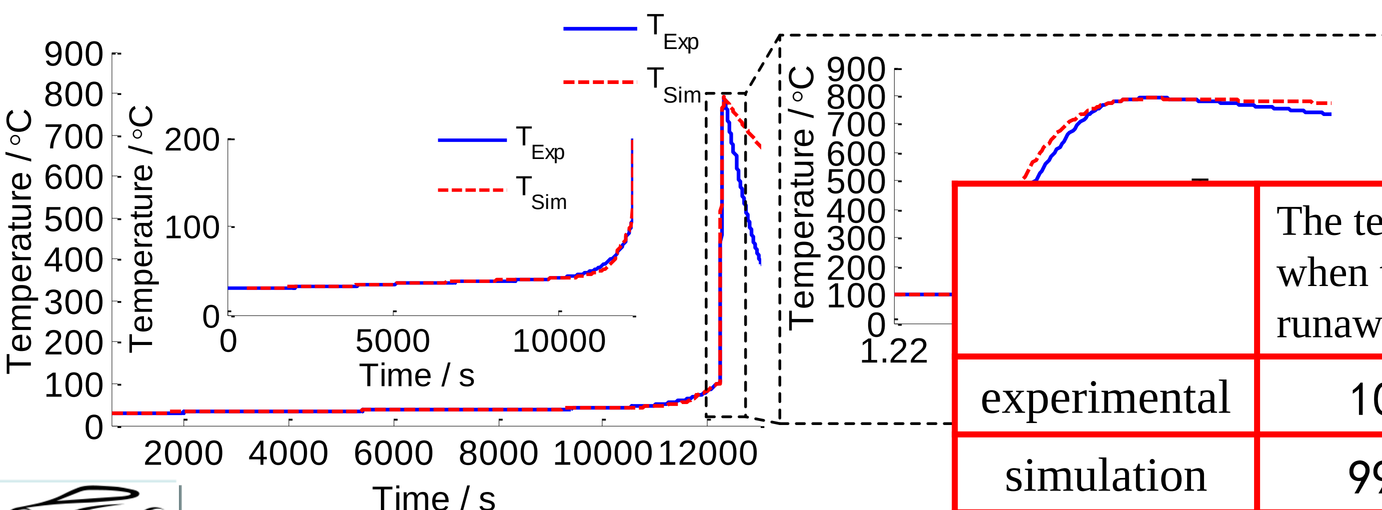
Joule heat ： $q=I^2Rt$

Heat generate by side reaction ：

Heat dissipation: $h(T-T_w)$

Side reactions	conditions
lithium metal deposited & electrolyte reaction	SOC>120%
electrolyte is oxidized and decomposed	SOC>138.8%
SEI decomposed	T>70℃
Anode react with electrolyte	T>120℃
Cathode decomposed	T>120℃



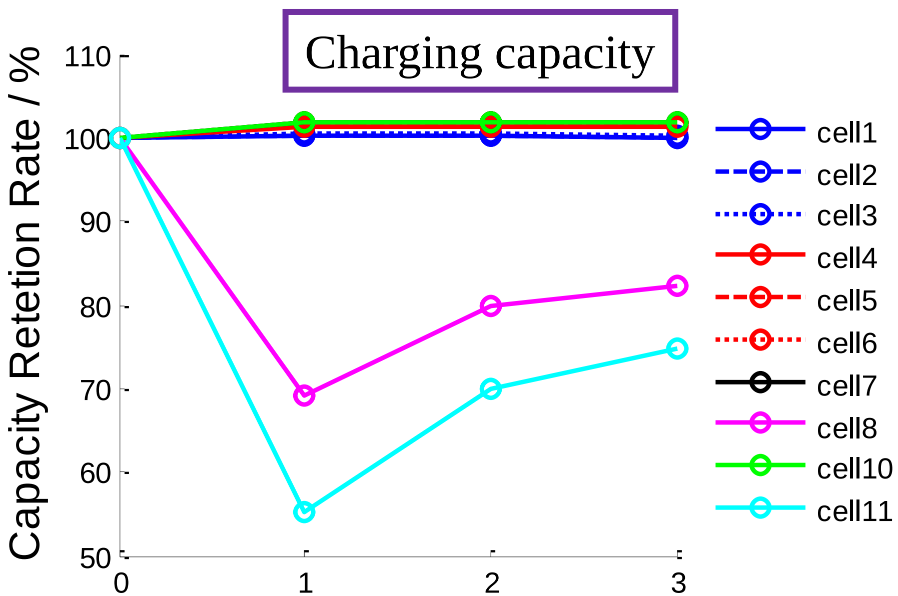


	The temperature when thermal runaway occurs	The maximum temperature
experimental	105.5℃	791.01℃
simulation	99.97℃	790.34℃

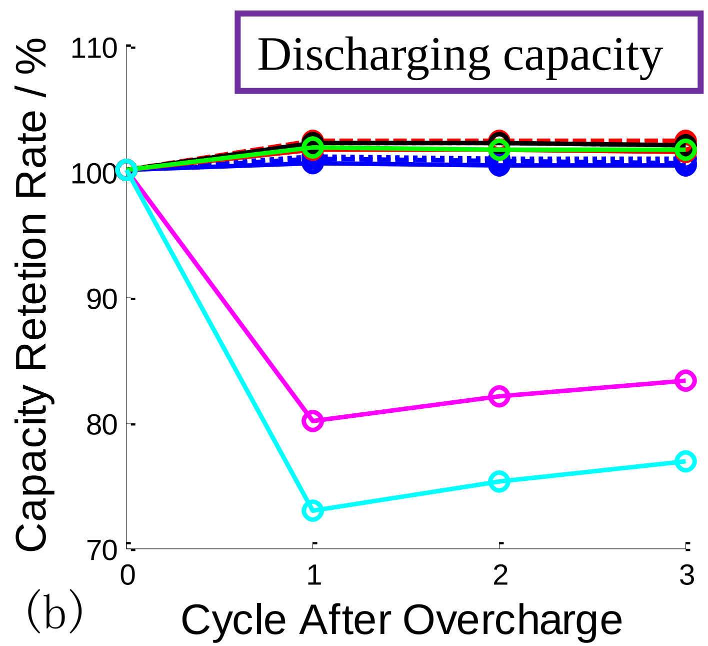
Cell degradation at different overcharge degree

- ➢Overcharge to SOC<130%, capacity no distinct degradation
- ➢Overcharge to SOC=138%, 150%, the capacity fade obviously.
- ➢Some of the capacity could be recovered after normal cycle.

Cell NO.	SOC
1~3, 10	110%
4~6	120%
7	130%
8	138%
11	150%



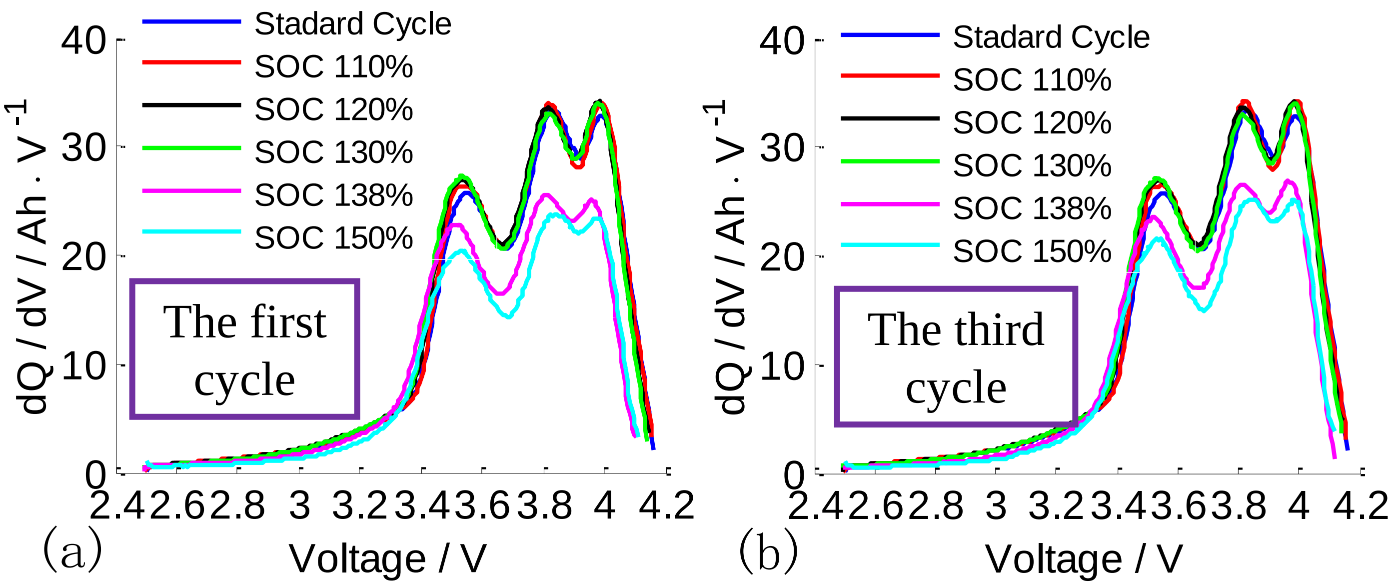
(a)



(b)

Cell degradation at different overcharge degree

The IC of the different overcharge degree

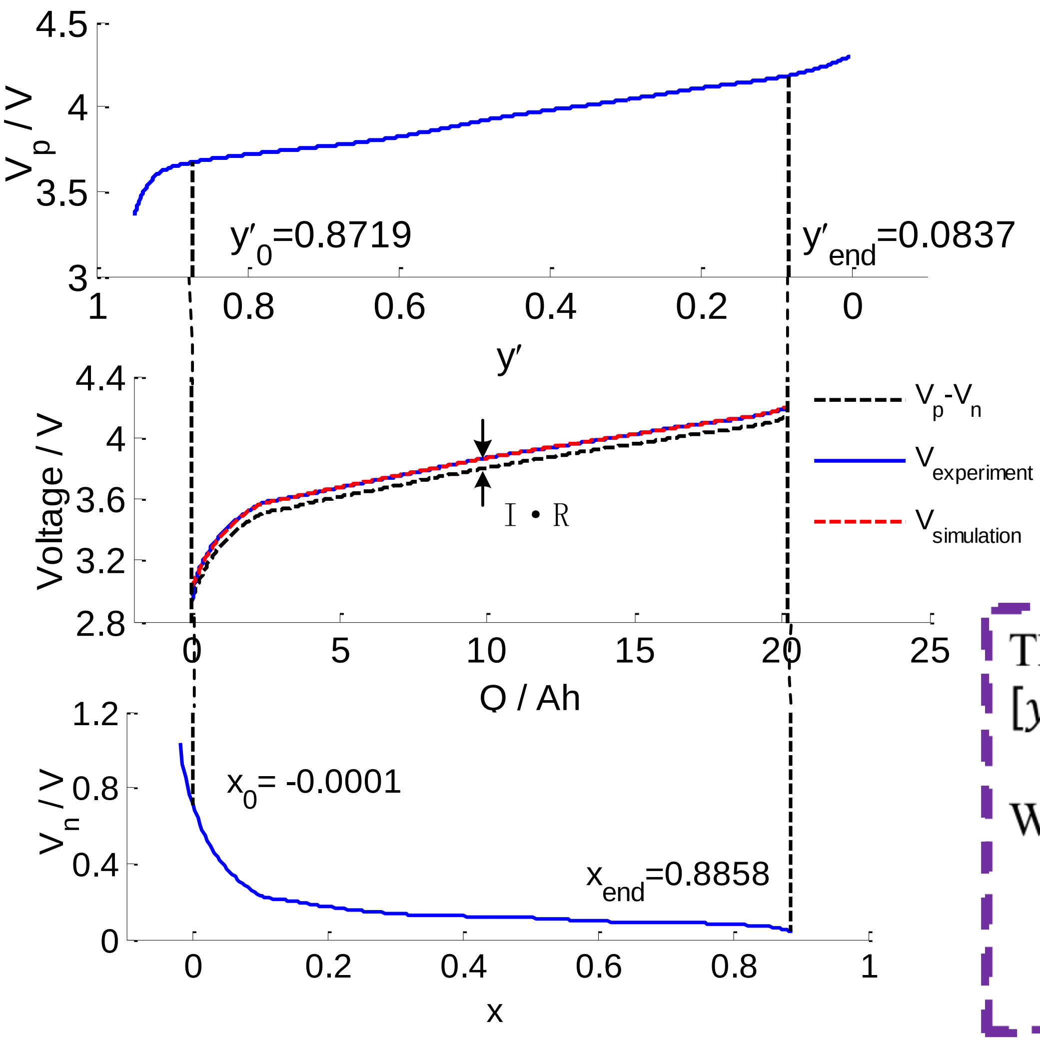


- ➢Overcharge to SOC<130%, IC is not change comparing with the normal charge's which mean the capacity of the battery is almost no loss.
- ➢Over charge to SOC=138%,150%, the height of IC decrease greatly which mean the capacity of the battery degrade dramatically.

[1].Han X, Ouyang M, Lu L, et al. A comparative study of commercial lithium ion battery cycle life in electrical vehicle: Aging mechanism identification[J]. Journal of Power Sources, 2014, 251: 38-54.

Cell degradation at different overcharge degree

Distinguish the performance fade with GA



$$V_{cha}(t) = V_p(y'(t)) - V_n(x(t)) + I \cdot R_{cha}$$

$$y' = y'_{0cha} - \frac{Q_{cha}}{C_{pcha}}$$

$$x = x_{0cha} + \frac{Q_{cha}}{C_{ncha}}$$

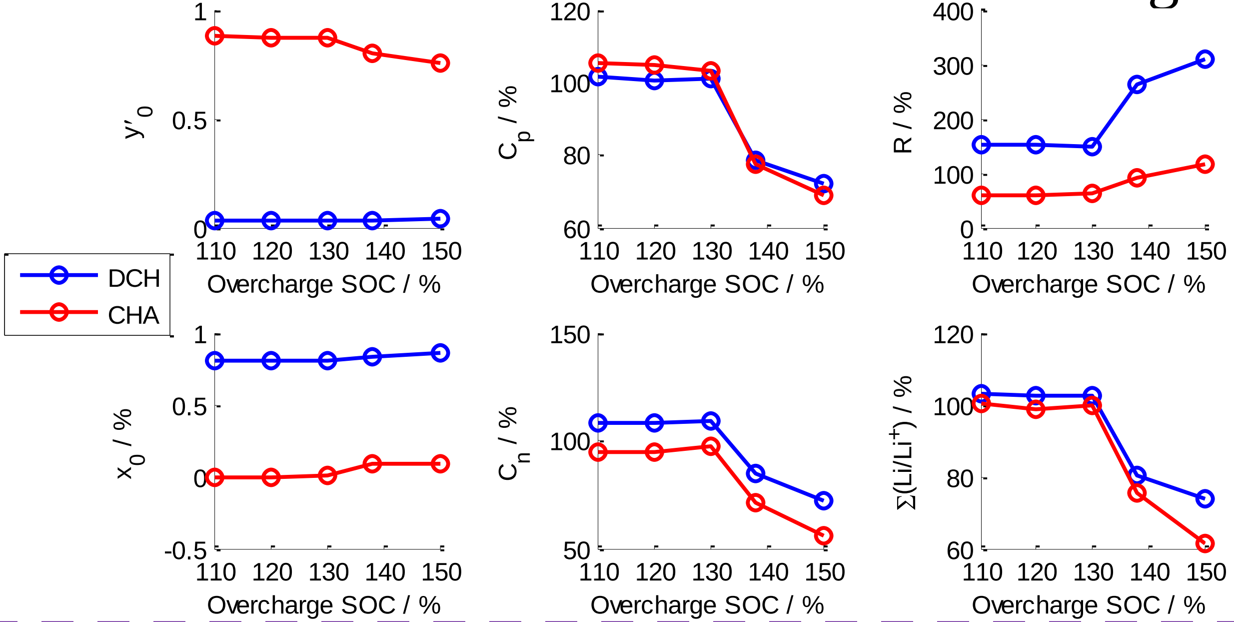
The parameters obtained by GA is $[y'_{0cha}\ ,\ C_{pcha}\ ,\ x_{0cha}\ ,\ C_{ncha}\ ,\ R_{cha}]$

Which lead RMSE is minimum.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(V_{cha}(t_i) - V_{cha}(t_i))^2}$$

Cell degradation at different overcharge degree

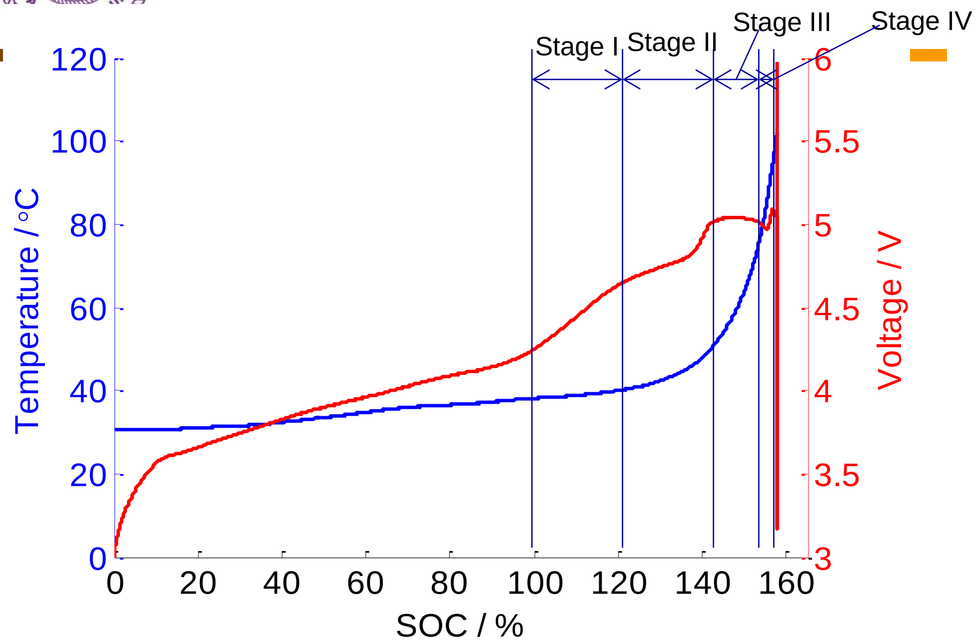
The parameters identified results at different overcharge degree.

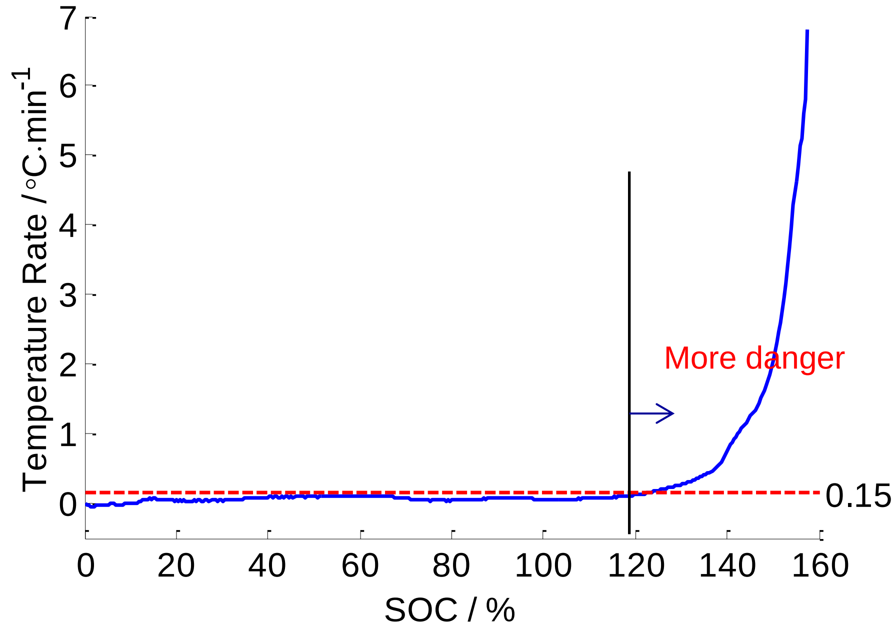


➢SOC<130%，the performance of the battery almost no fade after one overcharge；

➢SOC>130%, the performance of the battery fade after only one overcharge, the overcharge degree is higher, the degradation is serious. when overcharge to SOC=138%, both of the active material of anode and cathode loss 20%,the resistance of the battery increase to 220%. when overcharge to SOC=150%, both of the active material of anode and cathode loss 25%,the resistance of the battery increase to 270%.

conclusion

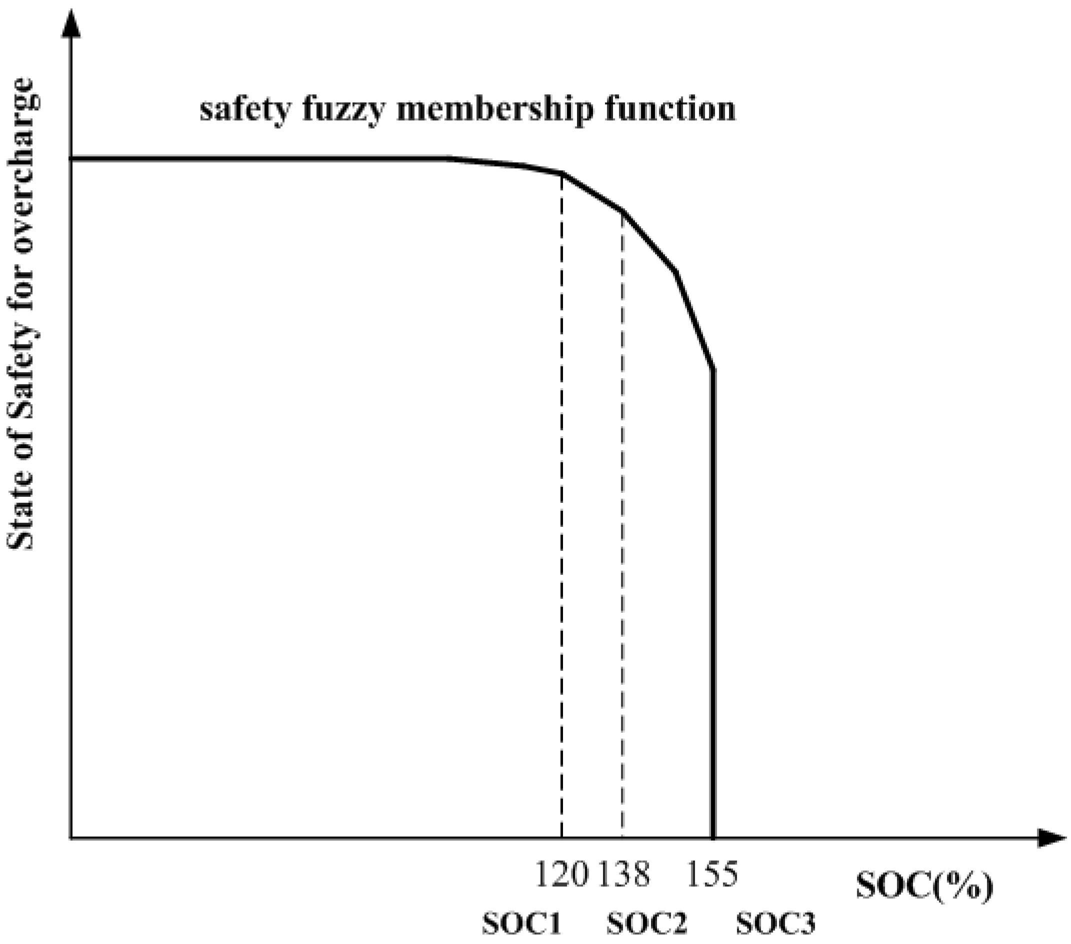




Stage I SOC=100~120% X=0.3346~0.1979	Satge II SOC=120~144% X=0.1979~0.0042	Stage III SOC=144~152% X<0.0042	Stage IV SOC=152~157.7%
• Battery has not yet irreversible structure changes . • Internal resistance is almost not change • Temperature rising is very slow, <0.15 ºC/min	• lithium metal begin to be deposited on the graphite anode • The temperature rate is rising • The structure of cathode is changing • The resistance is rising quickly.	•A voltage platform is appear •The electrolyte is oxidized and decomposed , generating a lot of heat and flammable gases •Battery swell seriously •The internal resistance decreases to the bottom at SOC146.5%, then increases quickly •Temperature rising quickly continuous (exponentially increase), >5 ℃/min	•The voltage drop a little, becomes unstable, then rises to the charger limited voltage, and then steep falls to 0V. •Temperature increases sharply, the temperature rise rate reach 6.8 °C/min before thermal runaway •Battery rupture. • Seriously short circuit and thermal runaway.

Future works

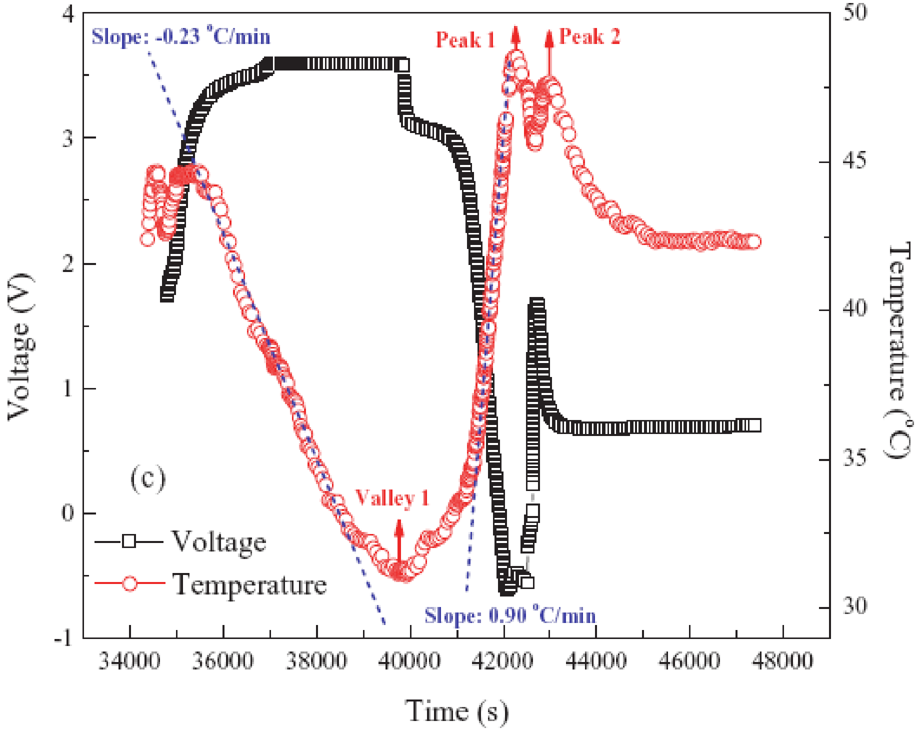
- Research on the overcharge thermal runaway under different C-rate charge, different environmental temperature.
- Improve the overcharge model of the thermal runaway
- Apply the overcharge SOS in BMS



Over discharge safety research

On-going

Over-discharge

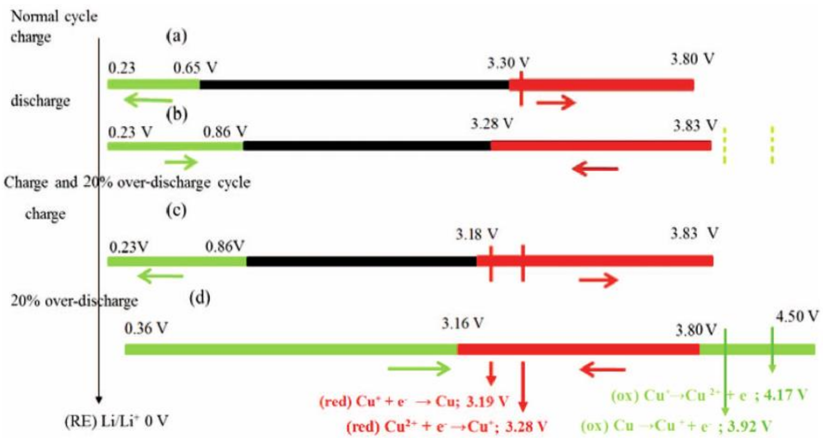


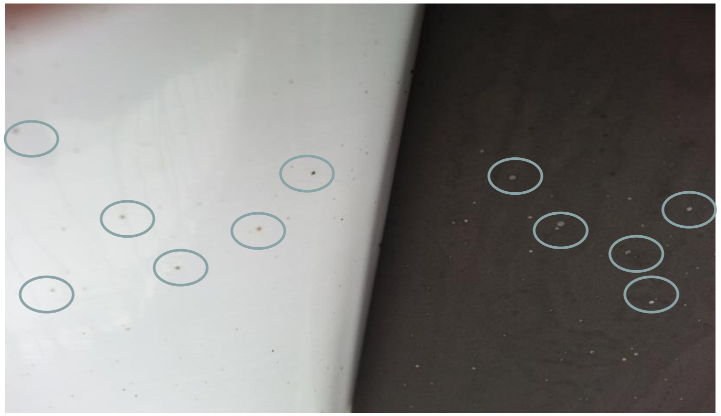
Oxidation : $Cu \rightarrow Cu^{+} + e^{-}$ 3.92 V (vs. Li/Li^{+}); [1]

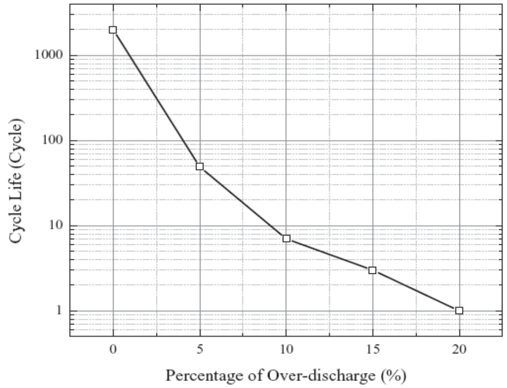
Reduction : $Cu^{+} + e^{-} \rightarrow Cu$ 3.19 V (vs. Li/Li^{+}); [2]

Oxidation : $Cu^{+} \rightarrow Cu^{2+} + e^{-}$ 4.17 V (vs. Li/Li^{+}); [3]

Reduction : $Cu^{2+} + e^{-} \rightarrow Cu^{+}$ 3.28 V (vs. Li/Li^{+}); [4]







PC **Figure 1.** Cycle life of commercial A123 18650 $LiFePO_4$ cells with different over-discharge cycle. Rate: 1 C. Room temperature.

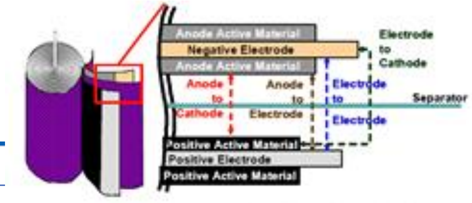
Hao He, Yadong Liu , et al, *Journal of The Electrochemical Society*, **160** (6) A793-A804 (2013)
Yadong Liu, Qi Liu, , et al, *Journal of The Electrochemical Society*, **161** (4) A620-A632 (2014)

Internal short circuit safety research

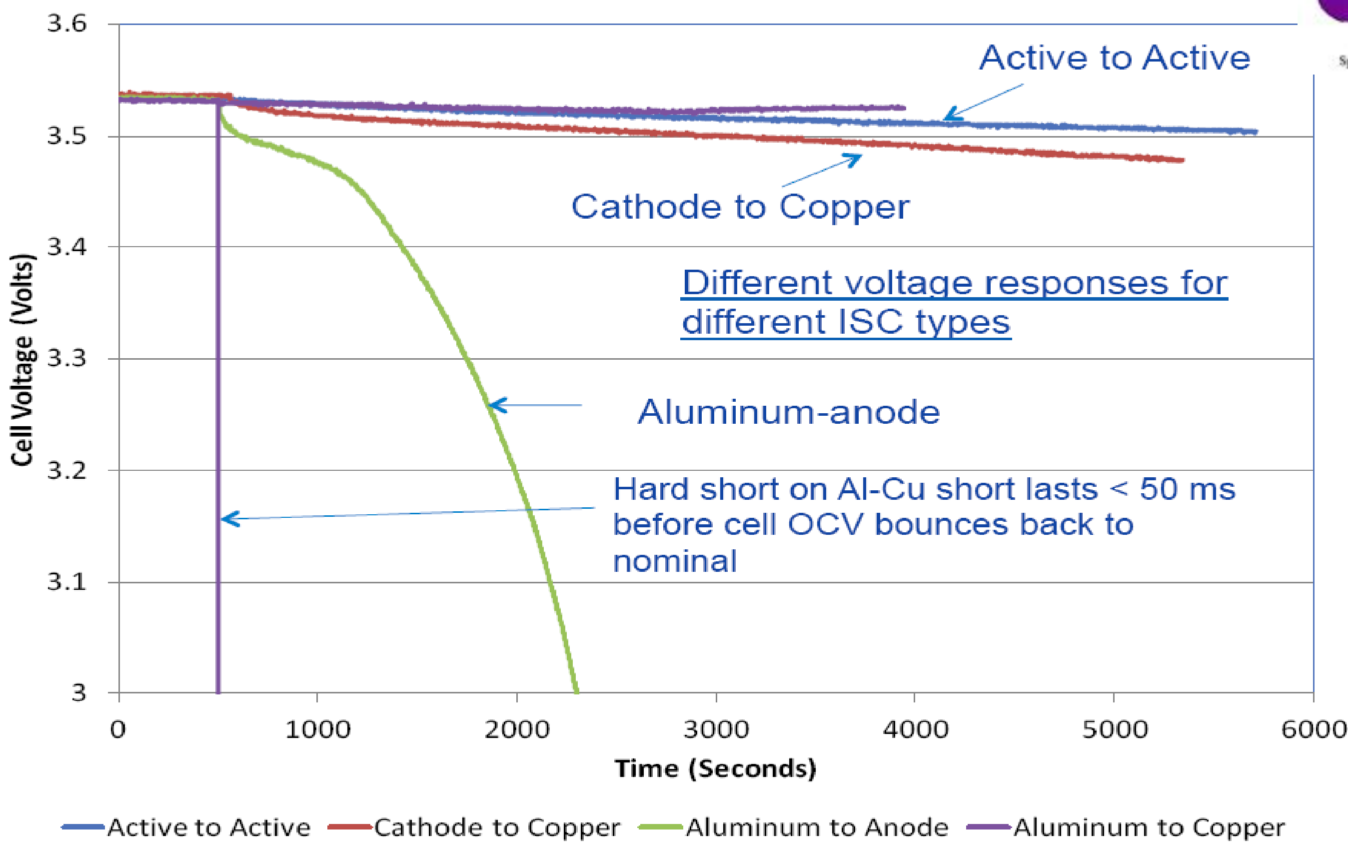
on-going

Internal short-circuit

DK 8 Ah Cell Activation at 10% SOC



Spiral wound battery shown – can also be applied to prismatic batteries.



Matthew Keyser, NREL/NASA internal short-circuit instigator in Lithium ion cells,
Battery safety 2013, November 14-15, 2013, San Diego, CA, USA,

Thank you for your attention!